[Contribution from the Muspratt Laboratory of Physical and Electro-Chemistry, the University of Liverpool]

THE THERMAL DECOMPOSITION OF OZONE. THE COMPUTATION OF VELOCITY CONSTANTS DETERMINED BY THE MANOMETRIC METHOD

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In a recent paper[1] on the thermal decomposition of ozone, Wulf and Tolman criticize our work[2] on the same subject. As part of their criticism appears to rest on a misunderstanding of the nature of the corrections which should be applied in such work, and as also the necessity for and magnitude of such corrections are not generally appreciated, we may be allowed to reply to their criticism and give a somewhat fuller account of our methods, together with their application to the experimental data of other investigators of this reaction.

In the first place, Wulf and Tolman take exception to the fact that the apparatus used by us to follow the decomposition at 100° contained "dead space"—the connecting lines from the reaction tube and the compensator tube to the manometer—which necessitated corrections to our pressure readings. This criticism might be pertinent if the "dead space" in question were large or the corrections improperly applied. Actually, however, the "dead space" in our apparatus was made reasonably small, the two tubes being joined directly through capillary taps to the sulfuric acid manometer, which was constructed of capillary tubing of 2 mm. internal bore. With the acid menisci level in the manometer, the volume unjacketed on either side was between 1.0 and 1.5 cc. in all our experiments. Finer capillary tubing for the manometer was avoided to obviate the risk of lag in the response of the manometer liquid to changes of pressure. As regards the condition that the reaction should take place at constant volume, this was sufficiently ensured, since a registered change of pressure of 200 mm. of sulfuric acid produced a change of volume of less than 0.4 cc. in a total of 150 cc. Indeed, the error involved in our measurements in this particular is considerably less than for the corresponding static experiments of Warburg[3] and of Jahn,[4] which, however, Wulf and Tolman view in a much less critical light. Thus with Jahn's apparatus, a change of pressure of 200 mm. of sulfuric acid would produce a change of volume of 0.078 cc. in a total of 6.3 cc.

Of much more importance, numerically, are the corrections to the registered pressure differences which the use of a moving manometric liquid

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[1] Wulf and Tolman, This Journal, **49**, 1183 (1927).

[2] Griffith and McKeown, *J. Chem. Soc.*, **127**, 2086 (1925).

[3] Warburg, *Ann. Physik*, **9**, 1286 (1902).

[4] Jahn, *Z. anorg. Chem.*, **48**, 260 (1906).

and the consequent variations in volumes of the "dead spaces" entail, and we have been at considerable pains to gage and apply these properly. Wulf and Tolman appear to associate the necessity for such corrections with poor technique; actually, however, similar but much greater corrections are necessary and were applied (though inadequately) in the work of Warburg and of Jahn. We proceed to indicate the nature and magnitude of these corrections.

The experimental arrangement commonly used consists essentially of a reaction and a compensator tube, capable of being jacketed at the same temperature, and connected to each other through a sulfuric acid manometer of capillary bore. We denote by V' and V'' the jacketed volumes of the reaction and compensator tubes, respectively, and by v the volume of unjacketed "dead space" on either side when the manometric levels are the same. If now with the whole apparatus at room temperature (Θ_1°, absolute) the manometer levels are identical, they will only be the same when the jackets are raised to the higher temperature Θ_2°, provided that $V' = V''$. Let us suppose that the tubes are filled at room temperature and to the same pressure (P_1 mm. of sulfuric acid), the one tube with the reaction mixture, the compensator with air or with oxygen. If a pressure difference of p_1 mm. of sulfuric acid, measured with the apparatus at room temperature, is subsequently developed due to reaction, the "true" increase of pressure which would have been developed, if measured, say, with a Bourdon Gauge, is not p_1 but $p_1\alpha_1$, where $\alpha_1 = 1 + \frac{P_1\gamma}{2}\left(\frac{1}{V'} + \frac{1}{V''}\right)$. Here γ is the volume in cc. per mm. of manometer tubing. However, an observed pressure difference of p_2 measured with the tubes at Θ_2° does not similarly correspond to a "true" increase of pressure of $p_2\alpha_2$, where $\alpha_2 = 1 + \frac{P_2\gamma}{2}\left(\frac{1}{V'} + \frac{1}{V''}\right)$, and P_2 is the total pressure (in mm. of sulfuric acid) in either tube at Θ_2°. That this is not so is due to the presence of "dead space" which is always at the lower temperature, Θ_1°. Neither is it true for the same reason that $(p_2\alpha_2/p_1\alpha_1)$ is equal to the ratio of absolute temperatures Θ_2/Θ_1. The only correct way of interpreting an observed pressure difference p_2 (measured with the tubes at Θ_2°) is to find the value of p_1 or of $p_1\alpha_1$, to which it corresponds at room temperature. This may be effected either by calculation from the equation

$$p_2 = \frac{\Theta_2\,(P_1 + \alpha_1 p_1)(V' + v)}{V'\Theta_1 + \left(v + \frac{p_2\gamma}{2}\right)\Theta_2} - \frac{\Theta_2 P_1\,(V'' + v)}{V''\Theta_1 + \left(v - \frac{p_2\gamma}{2}\right)\Theta_2} \qquad (1)$$

or the ratio p_2/p_1 may be determined experimentally. In our work, we employed the latter method, and values of the ratio p_2/p_1 under different experimental conditions are denoted by R in our tables.[5]

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[5] Ref. 2, pp. 2089–2091.

For our apparatus we found experimentally and have confirmed by independent calculation from (1) that the ratio p_2/p_1 under a given set of conditions is practically independent of the value of the registered pressure difference p_2. This implies that all corrections to our observed pressure readings affect only the absolute value of the derived velocity constants. The necessity for and use of corrections cannot be held responsible in our experiments for any observed "trend" in the value of a velocity constant throughout a single run. We may also remark that the conditions with regard to "dead space" in our apparatus were comparatively good (that is, $V' \Bumpeq V''$, and v and γ reasonably small compared with V'). In accordance with this we find that, had we employed the faulty method of correction used by Warburg and by Jahn (see next paragraph), the absolute values of our velocity constants would not have been affected by more than 4%.

Turning now to the work of Warburg and of Jahn, we must first note that their method of correcting their velocity constants to absolute units is equivalent to assuming that each observed pressure difference at Θ_2° corresponds to a true pressure difference of $p_2\alpha_2$ at the same temperature. This assumption is untrue; the more so as the "dead space" conditions in their experiments are considerably less favorable than in ours. We have attempted to estimate the errors thereby involved in their velocity constants in what follows.

The method of experimentation adopted by the two workers was the same, but slightly different from our own procedure. Their reaction and compensator tubes were first filled with oxygen to a known common pressure at room temperature Θ_1°. The oxygen in the reaction tube was then partially ozonized, the jacketing tubes raised to Θ_2° and the course of the reaction followed manometrically. Transforming again observed pressure differences p_2 at Θ_2° to the corresponding pressure differences p_1 which would be registered with the whole apparatus at Θ_1°, and hence to "true" pressure differences $p_1\alpha_1$ at Θ_1°, the relation now applying is

$$p_2 = \frac{\Theta_2 P_1\,(V'' + v)}{V''\Theta_1 + \left(v + \frac{p_2\gamma}{2}\right)\Theta_2} - \frac{\Theta_2\,(P_1 - p_1\alpha_1)(V' + v)}{V'\Theta_1 + \left(v - \frac{p_2\gamma}{2}\right)\Theta_2} \qquad (2)$$

In applying this equation to the data of Jahn and of Warburg, it is necessary to make some assumption regarding their values of v (the "dead space" on either side of the manometer). For both sets of measurements we have made the reasonable estimate that this volume corresponds to the volume of 25 cm. of the capillary tubing employed. This makes $v = 0.195$ cc. in Jahn's apparatus; $v = 0.135$ cc. in Apparatus VII of Warburg; and $v = 0.202$ cc. in Warburg's Apparatus III.

The correct velocity constant k_a expressed in the units (liters/moles-minutes) is then obtained by transforming all the observed pressure differences p_2 in a given experiment into the corresponding values of $p_1\alpha_1$, using $p_1\alpha_1 = 0$ as the infinity reading,[6] and substituting in the kinetic equation

$$k_a = 380 \times \frac{13.59}{1.84} \times 0.08207 \times \Theta_1 \times \frac{1}{(p_1\alpha_1)^2} \cdot \frac{d(p_1\alpha_1)}{dt} \qquad (3)$$

TABLE I

EXPERIMENTS OF JAHN

$\Theta_1 = 293°$, $\Theta_2 = 400°$, $V' = 6.281$ cc., $V'' = 4.233$ cc., $v = 0.195$ cc., $\gamma = 0.00078$ cc./mm.

Experiment A_I

$P_1 = 722 \times (13.59/1.84)$ mm. of sulfuric acid

t	p_2	$p_1\alpha_1$	k_a	k_a (Jahn)
1	124	247.4		
			62.2	93.3
2	98	201.5		
			84.7	136
3	75	160.9		
			46.0	79.3
4	66	144.9		
			57.3	104
5	57	129.1		
			55.3	107
6	50	116.7		
			55.8	120
8.3	38	95.5		
∞	—14.7*	0		
		Mean	60.2	106
				(108)

Experiment B_I

$P_1 = 539.1 \times (13.59/1.84)$ mm. of sulfuric acid

t	p_2	$p_1\alpha_1$	k_a	k_a (Jahn)
2	90	157.4		
			90.8	139
3	72	129.9		
			85.9	139
4	60	111.5		
			75.6	128
5	52	99.1		
			76.3	144
7	40	80.9		
			68.2	139
8	36	74.8		
			63.4	139
10	30	65.6		
			52.6	129
12	26	59.5		
∞	—12*	0		
		Mean (?)	73	137
				(140)

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[6] This follows from the fact that at room temperature and *before ozonizing* the oxygen in the reaction tube, the two tubes are at the same pressure.

TABLE I (*Concluded*)

Experiment C_I

$P_1 = 265.2 \times (13.59/1.84)$ mm. of sulfuric acid

t	p_1	$p_1\alpha_1$	k_a	k_a (Jahn)
1	54	70.8		
			179	275
2	44	59.6		
			143	235
3	38	52.9		
			151	260
4	33	47.3		
			147	266
6	26	39.5		
∞	—9*	0		
			Mean 155	259
				(258)

Considering first the data of Warburg for ozone decomposition, the "dead space" conditions are here not specially unfavorable, and recalculation of his results obtained with Tubes III and VII at 100°C. shows that his constants[7] are in each case about 10% too high. At the higher temperature, 127°, the correction is greater; his constants should be about 15% greater than those given. It is when applied to Jahn's data, however, that the corrections assume very large proportions. In order to demonstrate this, we have recalculated the constants in three of Jahn's experiments (A_I, B_I, C_I, pp. 289 and 290 of his paper). The results are shown in Table I.

In the preceding table, the first column gives the time in minutes, the second the observed pressure differences in mm. sulfuric acid, and the third the corrected pressure differences, $p_1\alpha_1$, which are calculated from the figures in Col. 2 by use of Equation 2. The fourth column gives the values of the corrected velocity constants in absolute units calculated from Equation 3, and the last column the velocity constants which would be obtained by calculation according to the methods employed by Jahn. In both cases the constants are computed over successive time intervals. The bracketed figures at the foot of each final column are the values of k_a obtained by Jahn by the method of least squares. Before comparing the corrected velocity constants with those of Jahn, it is first to be observed that Jahn's calculations are faulty, owing to the use of incorrect estimates of the final pressures. His reaction and compensator tubes were at the same pressure at *room temperature* before ozonizing the contents of the former, and since the volume of the reaction tube is considerably greater than that of the compensator, the presence of "dead

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[7] The values of all the velocity constants in absolute units given in Warburg's paper are ten times too small. The 10% correction mentioned above refers to (Warbrug's constants × 10).

space" clearly necessitates that the final pressure difference at 127° will *not* be zero, as assumed by Jahn, but will be of opposite sign to the pressure effect caused by ozonization. This is shown in the tables by the asterisked values of the infinity readings for p_2, which we have calculated by use of Equation 2. Errors in the value of p_∞ naturally affect the constancy of the calculated values of the velocity constants, and though this is partially disguised in Experiments A_I and C_I, it is fully revealed in Experiment B_I. Here the figures given in the final column, calculated with Jahn's assumption that p_2 at $t = \infty$ is zero, would appear to demonstrate an excellent bimolecular constant, but the figures in Col. 4 show that this agreement is fallacious and that proper correction gives a rapidly falling constant. In the other two experiments, the reaction was not followed for so long a time as in experiment B_I, and also there is a tendency for Jahn's constants to rise with time, both of which obscure the effect of correcting the infinity reading.

Comparing now Jahn's constants with the corrected ones, it is seen that his values in all three cases are of the order of 70–80% too high. It is not, however, our wish to lay any particular emphasis on the quantitative aspect of these figures, though we believe that they approximate to the true corrections necessary in his experiments; we desire simply to show that the published data of Jahn must be subject to quite large errors which are sufficient at least to render doubtful any conclusions drawn from his experiments by the manometric method. We draw attention to this, because Wulf and Tolman consider Jahn's experiments to demonstrate that "for ozonized oxygen which decomposes in accordance with the second order, the specific rate is closely inversely proportional to the total pressure." In our view, the uncertainties attached to Jahn's experimental data make any such conclusion of problematic worth.

We may summarize and compare the corrections necessary for "dead space" and moving manometric liquid in the experiments of Jahn, of Warburg and of ourselves in the following way. In our experiments the corrections necessary amount to and affect the observed velocity constants by between 7 and 22% depending on the total pressure; these corrections were properly applied. In Warburg's work the true corrections (for his experiments at 100°) amount to about 100%; the correction applied by him was somewhat less than this and leads to constants about 10% higher than those which should have been obtained. Finally, in Jahn's experiments the true correction lies between 200 and 95%, depending on the total pressure; the corrections actually applied by him were much too small, so that his constants are about 75% too high.

With regard to Wulf and Tolman's own experiments using the manometric method, they have applied no corrections to their pressure readings and in their paper they give no details of the dimensions of their manometer capillary. However, from a later (private) communication of Dr. Wulf, it appears that in the majority of their static experiments manometer tubing of diameter 0.87 mm. was employed. The volume of their compensator being 322 cc., the error due to non-application of the appropriate pressure corrections only amounts to about 2%.

These authors have also objected to our method of determining the final pressure increase corresponding to complete de-ozonization in each run. Admittedly small errors might enter here, but in all experiments pressure readings were taken up to between three-quarters and seven-eighths of total decomposition of the ozone initially present. Granting as a liberal estimate a 5% error in our determination of the pressure increase, which would be caused by decomposition of the residual ozone, the maximum error in our value of p_∞ is still less than 1%. Wulf and Tolman's own method of finding p_∞ is open to more serious criticism. After following the reaction for some time at 100°, they raise the temperature of the reaction vessel to 150° for fifteen minutes and assume that de-ozonization is then complete. Actually, for the Runs 10 and 15 which they give in detail in Table I (pp. 1189–90 of their paper), this is far from being the case. Taking their own value of the bimolecular velocity coefficient for ozone decomposition at 147.7°, namely, $k_2 = 1.3 \times 10^4$ cc./moles-sec., and noting that in Run 10 the extent of decomposition at this temperature corresponds to a pressure increase of 2.77 cm. of sulfuric acid, it is easy to calculate that there still remains, at the end of the fifteen minutes at 150°, a concentration of ozone equivalent to 0.60 cm. in the same units. This means that each value of the pressure difference P given in their Table I (Run 10) is 0.60 cm. too low. The large errors thereby involved may be appreciated from the following table, in which a number of the values of k_2 for Run 10 as calculated by Wulf and Tolman (Col. 4) are compared with the values (Col. 5) recalculated by us from the corrected pressure differences.

It will be observed that the corrected velocity coefficients are 12 to 22% less than those given by Wulf and Tolman, and also that the fall in the value of k_2 (corr.) with time is more pronounced. The true extent of this trend in the velocity coefficient is more correctly obtained by calculating the velocity coefficients *for successive time intervals* by the relation

$$k_2' = \frac{\text{const.}}{t_2 - t_1}\left(\frac{1}{P_2} - \frac{1}{P_1}\right)$$

instead of referring each coefficient back to the conditions at $t = 0$ as is done in using the formula

$$k_2 = \frac{\text{const.}}{t}\left(\frac{1}{P} - \frac{1}{P_0}\right)$$

The value of k_2' falls by about 33% while the concentration of ozone drops to one-third of its initial value.

TABLE II

t	P	P (corr.)	$k_2 \times 10^{-2}$ (W. and T.)	$k_2 \times 10^{-2}$ (corr.)	$k_2' \times 10^{-2}$
0	9.61	10.21	..	..	
					1.82
12	8.24	8.84	2.07	1.82	
					1.68
15	7.98	8.58	2.03	1.79	
					1.65
19	7.65	8.25	2.01	1.76	
					1.61
25	7.22	7.82	1.98	1.73	
					1.62
31	6.82	7.42	1.97	1.71	
					1.49
37	6.49	7.09	1.94	1.68	
					1.57
46	6.03	6.63	1.93	1.65	
					1.51
58	5.52	6.12	1.91	1.62	
					1.43
72	5.04	5.64	1.88	1.59	
					1.44
87	4.60	5.20	1.87	1.56	
					1.46
102	4.22	4.82	1.87	1.54	
					1.41
117	3.90	4.50	1.87	1.53	
					1.36
132	3.63	4.23	1.87	1.51	
					1.27
160	3.23	3.83	1.85	1.47	
					1.22
202	2.77	3.37	1.83	1.42	

In a private communication Dr. Wulf points out that we have probably overestimated the extent of the errors in his infinity pressure readings since (1) we have taken no account of the times necessary for heating the reaction system up to 150° and for cooling after the superheating, and (2) the value we take for k_2 at the temperature of superheating may be too low. Instead of 1.3×10^4, Dr. Wulf considers 1.9×10^4 to be a fairer estimate for k_2 at 150°, and he computes that 0.25 cm. is nearer the probable error in the final pressure of Run 10. Granted these possibilities, k_2' in Experiment 10 would then fall from 1.96×10^2 to 1.5×10^2 throughout the run.

Summary

The application by various workers of the manometric method to the investigation of the thermal decomposition of ozone is discussed. It is shown that the derived velocity constants may be in error through (*a*)

incorrect interpretation of the observed pressure differences and (*b*) faulty estimation of the pressure readings corresponding to total decomposition. Warburg's data are slightly in error under (*a*), Wulf and Tolman's data rather more seriously in respect of (*b*), while Jahn's results are subject to very considerable errors under both heads.

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[CONTRIBUTION FROM BELL TELEPHONE LABORATORIES, INCORPORATED]

THE DENSITIES OF COËXISTING LIQUID AND GASEOUS CARBON DIOXIDE AND THE SOLUBILITY OF WATER IN LIQUID CARBON DIOXIDE

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At the usually prevailing temperatures liquid carbon dioxide is less dense than water and not miscible with it. Therefore, theoretically, the degree of dryness of liquid carbon dioxide which has been separated mechanically from liquid water depends only on the solubility of the water in the liquid carbon dioxide. Experiments have been performed in an attempt to determine this solubility.

The method chosen was to determine the density of gaseous carbon dioxide in the coëxisting state, both in the presence and absence of water. If water is appreciably soluble in liquid carbon dioxide, it should lower the vapor pressure and hence the density of the coëxisting gaseous carbon dioxide. It may be calculated by means of Raoult's law that a solubility of 0.1%[1] by weight of water in liquid carbon dioxide will cause a decrease in vapor pressure of about 0.25%. The averages of three sets of determinations of the density of saturated gaseous carbon dioxide at temperatures ranging from —5.8 to 22.9° in the absence of water were 0.08% lower than the averages of two sets of determinations made in the presence of liquid water. This difference is opposite in sign to what would be expected if there were any solubility and is attributed entirely to experimental error.[2] The results obtained may be interpreted to indicate that the solubility of water in liquid carbon dioxide is less than 0.05% by weight over the temperature range investigated.

Experimental Method and Data

For the present investigation there was chosen the sealed tube method

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[1] This is an upper limit of the solubility as suggested by experiments performed by Thomas Simon, *Z. ges. Kohlensäure Ind.*, **6**, 239 (1900), and similar preliminary experiments performed by the authors.

[2] The average deviation of the experimentally determined gas density from the value calculated from the equation best fitting the entire data is 0.7%. Thus, while the probable error of any single datum is about 0.6%, consideration of the entire data indicates that the calculated values are probably correct within ±0.1%.