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Reconsideration of an Experiment on Water under Negative Pressure

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The experiment of Winnick and Cho on centrifuged water under inhomogeneous positive and negative pressure is re-examined. Several deficiencies in the data and analysis method are identified and corrected. A new, more complete theory of the experiment is derived and used to analyze corrected 20°C centrifuge data. From analysis of ordinary positive-pressure PV water data, it is established that best 20°C values of K_0, the bulk modulus at the vapor pressure of water, and K_0', the bulk modulus pressure derivative, are about 21 800 bar and 5.2, respectively. Least squares analysis of the Winnick–Cho data, on the other hand, shows that no meaningful estimate of K_0' can be obtained and that the $\hat{K}_0$ values derived are from about 11% to about 18% higher than the above expected value, depending on the detailed analysis approach. These unexpectedly large values of $\hat{K}_0$ appear to be highly statistically significant. It is concluded that they most probably arise from remaining systematic errors in the data, rather than from a still inadequate fitting equation or from significant differences in water properties on going from the positive pressure region to the low negative pressure region between zero and about -75 bar covered by the Winnick–Cho data.

I. INTRODUCTION

By means of an ingenious ultracentrifuge experiment, Winnick and Cho[1] (abbreviated hereafter as WC) have observed the inhomogeneous expansion of water under negative pressure. They state that theirs is the first successful investigation which measures the volume expansion of a liquid under negative pressure. Unfortunately, the negative pressure produced in their experiment and the resulting density decrease are continuous functions of position in the rotating capillary tube used, and neither average nor maximum negative pressures and density (or specific volume) changes are reported. It therefore becomes moot whether volume expansion has actually been measured by WC, even though the effects of some expansion have certainly been observed. Further, the volume expansion of a liquid under negative pressure has, in fact, been previously directly measured.[2,3]

The WC type of experiment is important, nevertheless, because of the light it may be able to shed on the detailed behavior of water in the negative pressure range if sufficiently high negative pressures may be reached in such an experiment. Unfortunately, there are defects in the WC data and detailed analysis which largely invalidate their results. Several of these defects will first be summarized here, then a more applicable analysis will be developed and used to analyze corrected WC data.

During my original analysis of the WC paper, I found that its data led to implausible values of water compressibility. When this result was communicated to WC, they discovered that a calibration factor of 2.165 had been omitted from all their published data and from the data in Cho's thesis[4] (on which the WC work was based). This omission, and the fact that the published data were smoothed, have now been acknowledged.[5]

In addition to the above problems, there seemed to me to be several further reasons why the theory and actual analysis of the experiment needed to be improved. First, WC's own analysis method is inaccurate since it is not properly based on water mass conservation and, even more important, it does not include the 6%–10% effect of capillary tube deformation under rotation. Next, WC did not consider the nonnegligible effects of thermal expansion of capillary tubes over their 5–35°C experimental range. Further, by using the two-parameter Tait equation of state rather than one more appropriate, WC unnecessarily complicated their analysis and failed to recognize that the precision of their data was only adequate to allow a single meaningful equation of state parameter—the bulk modulus or compressibility—to be estimated. In addition, the Tait equation used by WC to analyze outdated Amagat[6] PVT water data for the positive pressure region is inappropriate for the pressure range considered. Further, "Amagat" results were given for 25 and 35°C although Amagat presented no data at these temperatures. Finally, WC gave no standard deviations and quoted all their parameter estimates to five places, making one wonder how many places actually were significant.

II. THE POSITIVE PRESSURE REGION

A. High Pressure Range

The centrifuge experiment involves water under both negative and positive pressures. Thus, to obtain results for comparison with those of WC for the positive-pressure region, I shall analyze the conventional P–V water data of Kell and Whalley[7] (abbreviated KW), which involve 27 points covering the pressure range from about 5 bar to 1 kbar. Their data for $T=19.997$°C will be used since WC give their own main results for 20°C. The KW data set is certainly the most precise currently available for water and is

TABLE I. Results of C weighting, generalized least squares fitting of Kell–Whalley 19.997°C water data.[7]

Line	Equation	N	s_d	$\hat{V}_0$ (cm³/g)	$\hat{K}_0$ (bar)	$\hat{K}_0'$	$\hat{\psi}$
1	Tait	27	3.76	$1.001849 \pm 2\times10^{-6}$	21 698±9	5.93±0.02	···
2	3DGE	27	1.68	$1.001840 \pm 1\times10^{-6}$	21 796±8	5.20±0.05	37.9±3.2
3	3DGE	9	1.33	1.001840 (F)	21 767±15	7.06±0.37	−782±93
4	2DGE	9	1.25	1.001840 (F)	21 790±16	5.51±0.40	···
5	Tait	9	1.25	1.001840 (F)	21 790±3	5.48±0.07	···
6	VQE	9	1.25	1.001840 (F)	21 793±14	5.31±0.33	···
7	DQE	9	1.26	1.001840 (F)	21 792±26	5.39±0.63	···

probably also the most accurate as well.[8] All equations of state used herein are given in the Appendix.

Using Amagat's 1893 data,[6] covering the range from 1 to 10^3 atm, WC obtained 20°C positive-pressure Tait parameter values of $B^+ \cong 2790.4$ bar and $K^+ \cong 0.13041$ cm³/g. The WC results and those herein have all been calculated using the reference pressure P_0, which appears in the equation of state, taken equal to the saturated vapor pressure of water, P_V. For $T=20$°C, $P_V \cong 0.02338$ bar.

The KW data, analyzed by applying weighted nonlinear least squares to the usual Tait equation, yields $\hat{V}_0=(1.001849\pm2\times10^{-6})$ cm³/g, $\hat{B}^+=(3133\pm 12)$ bar, and $\hat{K}^+=(0.1446\pm0.0005)$ cm³/g. Here V_0 is the specific volume at $P_0=P_V$, and standard deviations are shown for each of the parameter estimates. Note the considerable uncertainty in the present B^+ and K^+ parameter estimates, even though the excellent KW data themselves are given to six places in specific volume. These estimates were obtained using a newly improved, generalized least squares procedure[8,9] which allows simultaneous weighting of both the dependent and the independent variable to be employed. The "C" weighting of an earlier analysis of 0°C KW data[8] was used, since this weighting was there found to be most appropriate for the data. It results in the squared volume residuals contributing about 64% to the final sum of squares and the squared pressure residuals about 36%; for the later results shown in lines 3–7 of Table I, the corresponding percentages were about 80% and 20%. Conventional constant weighting of either pressure or specific volume values led to parameter estimates within a few standard deviations of those above. All the least squares fitting of the present paper was carried out using an IBM 360–85 computer in double precision mode.

The differences between the WC and KW parameter estimates are 30 standard deviations of the KW estimates or more. Such large differences indicate the certain presence of systematic errors, here in the Amagat data and/or in the WC fitting procedure. It is important to note, however, that the values of B^+/K^+ which follow from the two sets of estimates are nearly the same. Since this ratio is very nearly proportional to the physically significant, first-order parameter of all equations of state, the reference-pressure bulk modulus, it is not surprising that different fitting results should yield close agreement for estimates of this parameter.

Since WC also find, on analyzing their centrifuge experiment, B^- and K^- parameter values quite close to their above positive pressure results, it seems worthwhile to establish to what degree their anomalously low values arise from inaccuracies in the Amagat data or from the nonlinear regression fitting process they used in analyzing these data. Therefore, I have carried out an ordinary nonlinear least square fitting of the 20°C Amagat data (with an obvious misprint corrected) using the ordinary Tait equation with V_0, B^+, and K^+ take as free parameters.

The Tait fitting of the Amagat 20°C data was performed in the conventional way with ordinary (unity) weighting of the squared specific volume residuals and with the pressure values of the data taken as exact. The standard deviation of fit obtained was 2.6×10^{-5} cm³/g and $\hat{V}_0=(1.001625\pm9\times10^{-6})$ cm³/g, $\hat{B}^+=(3052\pm28)$ bar, and $\hat{K}^+=(0.1408\pm0.0011)$ cm³/g. Since these values differ scarcely more than three of their own standard deviations from the above KW data results, it appears that the WC data fitting method itself primarily led to the relatively low values of B^+ and K^+ these authors present.

It has already been pointed out[8,10] that the B and K Tait parameters are not physically very meaningful and that the Tait equation may be better written in terms of the easily interpretable first and second order parameters K_0 and K_0'. When we define the ordinary bulk modulus of the material as $K \equiv -V(\partial P/\partial V)_T$, K_0 is the value of K (*not* the WC K parameter) at $p \equiv P-P_0=0$, and $K_0' \equiv (\partial K/\partial P)_{T,p=0}$, a dimensionless parameter usually from 3 to 10 in value. The 19.997°C KW data lead to the C-weighting Tait-equation parameter estimates shown in line 1 of Table I. Of course, $\hat{V}_0$ and the standard deviation of fit are exactly the same as the above KW values found using B and K parameters. Here s_d is the over-all standard deviation of the fit. The mean of its distribution should be slightly below unity for the correct model and proper weighting. The considerably larger value here indicates the likelihood of a poor fit. The quantity N is the number of data point pairs.

WC were evidently unaware that the usual Tait equation itself, when applied to modern water data covering a pressure range of several hundred bars or more, leads to a much worse fit than do some higher-order equations of state which involve more free parameters than does the Tait equation.[8] For example, the Tait equation fit yields strong systematic errors in the residuals obtained from the fitting of either KW or Amagat data. Such systematic errors, arising from a wrong equation or model choice,[11] are only eliminated or adequately minimized when either a higher-order equation is employed[8] or the maximum pressure is much smaller. Thus, parameter estimates obtained from Tait equation fitting of water data extending to 1 kbar may be expected to show appreciable systematic wrong-model-choice errors.

This effect may be demonstrated by fitting the KW 19.997°C data with the higher-order 3DGE polynomial equation of state,[8] which leads to negligible apparent systematic errors in the residuals. Again using C-weighting, one obtains the results of line 2 of Table I. Here, we have introduced the higher-order dimensionless parameter $\psi \equiv K_0 K_0''$, and $K_0'' \equiv (\partial^2 K/\partial P^2)_{T,p=0}$. The differences between these estimates of K_0 and K_0' and the Tait equation estimates largely arise from systematic errors introduced by the use of the inappropriate Tait equation.

The various parameters of the 3DGE enter nonlinearly, as do those of the Tait equation. The parameter and standard deviation estimates obtained from least squares fitting with these equations are thus biased.[8,9,11] But we may readily show that the 3DGE parameter estimates are only negligibly biased in the present situation. The 3DGE may be written in terms of a new set of parameters which *do* enter linearly[11] (see Appendix). Estimates of these new parameters may then be combined to yield values of the usual parameter set of Table I. Since linear least squares fitting yields unbiased estimates, we thus have a test of the original nonlinear estimates. The $\hat{V}_0$ value obtained from linear fitting is the same as that of line 2, Table I to six decimal places; the other parameter estimates differ from those of the table by only 10^{-3} of their corresponding standard deviations. Actually, C-weighting itself destroys the strict linearity of linear least squares fitting,[8,9] but similar close results are obtained with ordinary weighting of the pressure values alone (the "dependent" variable in the 3DGE). Since the 3DGE results of line 2 involve no obvious systematic errors in the residuals and are unbiased for practical purposes, these values may be taken as best available estimates for the 20°C parameters.

B. Low Pressure Region

The maximum negative pressure attained in the WC experiment was only about 75 bar. Now that we have obtained adequate parameter estimates from the 0–1 kbar data, it is important to investigate how closely various equations of state can come to yielding these same estimates when applied to accurate positive-pressure PV data extending only up to 75–100 bar. In this way we can (a) better select an equation of state appropriate for this region, and (b) obtain some actual information on the uncertainties of K_0 and K_0' parameter estimates derived from such low pressure data. This information will also be valuable in assessing the result of fitting the WC data.

Again, we shall use the 19.997°C KW data, selecting only the first nine low-pressure data points, up to and including that at about 101 bar. C-weighting will again be used, and this time V_0 will be taken known and fixed at the Table I, line-2 value for all the fitting. Such fitting of V_0 is indicated by the letter "F" in the $\hat{V}_0$ column. Thus, here and in the subsequent WC data fitting, only K_0 and K_0' values will be estimated.

Let $z \equiv p/K_0 \equiv (P-P_V)/K_0$, a normalized pressure variable. Now as z decreases much below unity, all equations of state begin to coalesce. In the present WC situation, the maximum magnitude of z, $|z_m|$, is only about 3×10^{-3}. Thus, it appears that it shouldn't make much actual difference which equation is selected for this region. In fact, it turns out that to terms of order z^2 all equations of interest, including the Tait, Murnaghan, and even those such as the 3DGE involving higher-order parameters, exhibit the same series expansion, namely,

$$(V/V_0) = 1 - z + (K_0'+1)z^2/2, \qquad (1)$$

an equation of state we shall term the VQE, for volume quadratic equation. Taking $K_0' = 5.2$ and $z = z_m \cong -3.37\times10^{-3}$, the z^2 term above becomes about 3.5×10^{-5}, and higher-order terms in z will be quite negligible for even data with six decimal digits in V, such as that of KW. From a theoretical point of view, it will thus be just as adequate here to use the quadratic approximation to $(V_0/V) \equiv (\rho/\rho_0)$ following from Eq. (1), namely

$$(\rho/\rho_0) = 1 + z - az^2, \qquad (2)$$

where $a \equiv (K_0'-1)/2$ and ρ is the density. This result of course also follows from direct expansion of the various equations of state to this order. I shall term this equation of state the DQE, for density quadratic equation.

While the Tait, 3DGE, VQE, and DQE are all theoretically equally applicable in this low-pressure region, the DQE simplifies the subsequent analysis the most and will therefore be used. The Tait equation is too complicated in form to allow all the quadratures involved to be obtained in closed form. Thus, part of the fitting procedure used by WC necessarily involved numerical quadrature, and they were unable to fit using the same free equation of state parameters for both the positive and negative pressure regions. Though the above equations, and the 2DGE, a lower order version of the 3DGE, all lead to Eq. (2) when expanded in powers of z to z^2 terms, it is still of interest

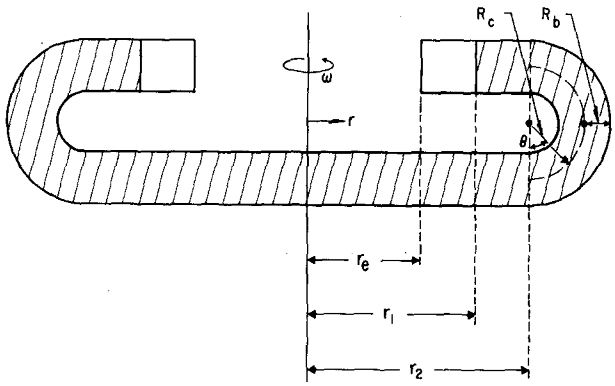

FIG. 1. Diagram of filled capillary tube showing axis of rotation and pertinent length designations.

to see how well they all agree in estimating K_0 and K_0' from the 9-point KW data. The results of C-weighting, least squares fittings are shown in Table I, lines 3–7, All fittings led to the same residual sign pattern, namely $-+-+---+-+$, which shows no long-period systematic behavior.

The results in line 3 indicate that the 3DGE is a poor model choice for these low pressure water data. As the Appendix shows, the right hand side of the 3DGE is a polynomial of third degree in $w \equiv (V_0/V)-1$. The w^3 term, where ψ enters, should be negligible compared to the w^2 term in this pressure region. Instead, $\hat{\psi}$ is so large in magnitude that the two terms are comparable in magnitude. Further, they turn out to be opposite in sign. The exceedingly poor estimate for ψ clearly forces the other parameter estimates to be poor as well.

As line 4 shows, the results obtained with the 2DGE, which involves terms up to only w^2, are much improved. The values given in lines 4–7 show that all the parameter estimates are close to those of line 2. In fact, except for the Tait results, all parameter estimates are well within one of their own standard deviations of the corresponding line 2 values. Additional least squares fits of the 2DGE and VQE, written in terms of new parameter sets entering linearly, again yield derived parameter estimates within a small fraction of a corresponding standard deviation of those obtained directly and listed in Table I. Thus, parameter bias because of nonlinear least squares fitting is not likely to be a factor here.

The various standard deviation estimates show much greater variability. These results are calculated in the usual way[8] with a linearizing approximation by the same formula which is used for linear least squares problems. Thus, the standard deviation estimates are possibly significantly biased, especially those in line 5 for Tait fitting. The relative importance of bias and sampling error cannot be directly assessed here, however. Nevertheless, there seems to be a definite trend for Tait-equation fitting to yield strongly biased standard deviation estimates that are much too small.

III. IMPROVED ANALYSIS

A. Pressure–Distance Relation

The WC experiment involves C-shaped capillary tubes, partly filled with water as in Fig. 1, spun horizontally about their axes of symmetry, an approach used earlier by Briggs.[12] During rotation, water in a considerable part of the tube under tensile force is balanced by water under compression. Under constant mass conditions net expansion of water leads to a movement of the water meniscus in each leg of the C toward the axis of rotation, thus reducing r_1, the distance to the meniscus in the upper leg of the tube.

To calculate the pressure as a function of r, one must solve the basic hydrostatic equation

$$dP/dr = dp/dr = \rho(P)\omega^2 r, \tag{3}$$

where ω is the rotation rate. Solution of this equation requires an equation of state. Here I shall use the DQE for reasons already discussed. The equilibrium density, ρ_0, applying at 19.997°C and $P=P_V\cong 0.02338$ bar, will be taken as the known constant $V_0^{-1}\cong 0.998163$ g/cm^3.

If we now express Eq. (3) in terms of z and use (2), we find, after a lengthy calculation

$$z=2\tanh[\phi\Omega(r^2-r_1^2)]/\{2\phi-\tanh[\phi\Omega(r^2-r_1^2)]\}, \tag{4}$$

where $\phi\equiv(1+4a)^{1/2}/2$ and $\Omega\equiv\rho_0\omega^2/2K_0$. Note that r_1 is a function of ω. Since the argument of the tanh terms is always small in the present experiment, expansion yields

$$z\cong\Omega(r^2-r_1^2)+[\Omega(r^2-r_1^2)]^2/2\cdots, \tag{5}$$

showing that K_0' appears only in the omitted, higher order terms. The use of the VQE instead of the DQE in Eq. (3) also leads to Eq. (5) to the order shown. Since the maximum value of ω used by WC was 600π rad/sec, the maximum value of Ω, Ω_m, turns out to be about 8.134×10^{-5} cm^{-2} when one uses $K_0\cong 2.18\times10^4$ bar and $\rho_0\cong 0.99816$ g/cm^3. The maximum magnitude of z occurs at $r=0$. Taking $(r_1)_{\omega=\omega_{\max}}\equiv r_{1m}$ as 6.44 cm, essentially its maximum value, we find $z=z_m\cong -3.37\times10^{-3}+5.7\times10^{-6}\cdots$. Clearly, the series for z may be truncated after the second term, as in Eq. (5), with no important loss of accuracy.

The maximum negative pressure corresponding to z_m is $P_{nm}=P_V+K_0z_m\cong-73.4$ bar. This value is comfortably smaller in magnitude than the maximum negative pressure of about -270 bar found by Briggs[3,12] where water cavitates. Thus, the experiment should lead to no open vapor-filled region in the capillary centered around the axis of rotation.

WC used the following approximate expression in place of (4) or (5)

$$z_{WC}=\Omega(r^2-r_1^2)[\bar{\rho}_P/\rho_0], \tag{6}$$

where

$$\frac{\bar{\rho}_p}{\rho_0} = \int_0^{r_1} r dr \bigg/ \int_0^{r_1} r \frac{\rho_0}{\rho} dr. \qquad (7)$$

This result is adequate for data which only allow a first-order parameter to be estimated but inadequate when two parameters are estimated as WC did. Although the corrected WC data only support the estimation of K_0, not K_0' as well, K_0' terms will be retained in the theoretical analysis. This approach will allow K_0' to be estimated when more precise data become available and will also allow me to show to what degree such estimation fails for the WC data.

B. The Liquid Mass Equation

When Eq. (5) is substituted in (2), one obtains for the density ratio

$$[\rho(r)/\rho_0] = 1 + \Omega(r^2 - r_1^2) - b[\Omega(r^2 - r_1^2)]^2, \qquad (8)$$

where $b \equiv (K_0' - 2)/2$. For $\Omega = \Omega_m$, $r_1 = 6.44$ cm, and $b = 1.6$, we obtain the minimum density ratio

$$[\rho(0)/\rho_0] = 1 - 3.37\times10^{-3} - 1.8\times10^{-5} \cong 0.99661, \quad (9)$$

with the next omitted term being less than 10^{-7} in magnitude. Note that K_0' appears only through the b term in Eq. (8), which here contributes a maximum of only about 2 parts in 10^5 to the density ratio. The unsmoothed Cho data[4] for $\Delta r \equiv r_1 - r_{1m}$ have a resolution of 10^{-4} cm and an estimated experimental error of 6×10^{-4} cm. Since errors in Δr may be as large as 1 part in 30, it is quite clear that no meaningful K_0' esimates can be obtained from these data.

Since none of the WC capillary tubes is entirely symmetric around the axis of rotation, the analysis should account for this asymmetry by appropriate averaging. The effect is relatively small, as shown by the data of Table II, and was implicitly ignored by WC. I shall include it in the actual fittings herein but, for simplicity, omit it from the following analysis. The r_{1m} values of Table II were kindly provided directly by Cho. The Δr data[1,4] to be analyzed are for 20°C, sufficiently close to room temperature that no thermal corrections need be made in the data of Table II.

Analysis of the ultracentrifuge experiment requires an expression for $\Delta r(\omega)$. Since the total water mass M_0 in a sealed capillary tube is independent of ω, a general expression for M_0 evaluated at two different ω values may be used to obtain $\Delta r(\omega)$. Convienent values would be $\omega = 0$ and $\omega = \omega$, but, unfortunately, WC did not measure M_0 at $\omega = 0$. Thus, it is necessary to employ $\omega = \omega$ and $\omega = \omega_m$, using up the $(\Delta r_m, \omega_m)$ data pair in the process. To obtain M_0 itself, it is most convenient to integrate (ρ/ρ_0) over all water-containing regions of the capillary, taking account of all liquid mass elements lying on disk-shaped planes of area $A \equiv \pi R_b^2$, and of perpendicular distance r_p from the axis of rotation. Since R_b deforms during rotation, A is not the constant implicitly assumed by WC. Let the $\omega = 0$ values of R_b and A be denoted by R_{b0} and A_0. Then ignoring the miniscule change in liquid mass arising from the change of vapor phase mass when Δr changes and any deformation in bore shape, $N_0 \equiv M_0/2\rho_0 A_0$ is given exactly by

TABLE II. Pertinent dimensions (in centimeters) for three capillary tubes[1] at room temperature. The "l" and "r" subscripts denote left and right sides.

Dimension	Tube No. 7	Tube No. 51	Tube No. 58
R_b	0.025	0.045	0.045
R_{cl}	0.4348	0.4395	0.4675
R_{cr}	0.4330	0.4411	0.4660
r_{2l}	7.8064	7.8631	7.8276
r_{2r}	7.8082	7.8615	7.8291
r_{1m}	6.3854	6.3883	6.4436

$$N_0 = I_1 + 2(I_2 + I_3), \qquad (10)$$

where

$$I_1 \equiv \frac{4}{A_0} \int_0^{r_1} \int_0^{R_b} [R_b^2 - x^2]^{1/2} \left(\frac{\rho(r_a)}{\rho_0}\right)^- dx dr, \quad (11)$$

$$I_2 \equiv \frac{4}{A_0} \int_{r_1}^{r_2} \int_0^{R_b} [R_b^2 - x^2]^{1/2} \left(\frac{\rho(r_a)}{\rho_0}\right)^+ dx dr, \quad (12)$$

and

$$I_3 \equiv \frac{2R_c}{A_0} \int_0^{\pi/2} \int_{-R_b}^{R_b} \int_0^{[R_b^2 - y^2]^{1/2}} \left(\frac{\rho(r_c)}{\rho_0}\right)^+ dx dy d\theta. \quad (13)$$

In these integrals $r_p = r_a \equiv [r^2 + x^2]^{1/2}$ and $r_p = r_c \equiv [x^2 + \{r_2 + (R_c - y)\sin\theta\}^2]^{1/2}$.

WC were only able to derive estimates of equation of state parameters from their data for the negative pressure region, $0 \le r < r_1$. For greater generality, it is desirable to be able to use the same or different parameters for the positive and negative pressure regions. Therefore, define $K_0^\pm$, $K_0'^\pm$, $b^\pm$, $\Omega^\pm$, and $(\rho/\rho_0)^\pm$ for the positive and negative pressure regions. Then the (ρ/ρ_0) of I_1 becomes $(\rho/\rho_0)^-$ and those of I_2 and I_3 become $(\rho/\rho_0)^+$ as shown.

Unfortunately, the exact evaluation of N_0 is complicated when R_b varies with r and ω. Let $\Delta \equiv \Delta R_b/R_{b0} \equiv (R_b - R_{b0})/R_{b0}$. Now for maximum tube deformation under rotation $|\Delta| \ll 1$. Further, for $R_b \ll r_1$ the effect of ignoring the distinction between r_p and r, implicit in the WC approach, is also small. The difficulty arises in accounting exactly for the interaction of these two small effects. Let us therefore ignore the product interaction, which in cases of interest will be smaller than second order in N_0. We may still account for the effects separately as follows. Define $\epsilon \equiv (\rho/\rho_0) - 1$, and note that $|\epsilon| \ll 1$. When $r_p \to r$, Eqs. (10)–(13) are replaced by

$$\begin{aligned} N_0 &\cong \int [A(r)/A_0][\rho(r)/\rho_0] dr \\ &= \int [(1+\Delta)^2(1+\epsilon)] dr \cong \int [1 + \epsilon + 2\Delta] dr \\ &= \int [\{\rho(r)/\rho_0\} + 2\Delta(r)] dr, \end{aligned} \qquad (14)$$

where the integral is taken over all water-filled regions and again higher-order coupling terms have been neglected in the final result. Note that the first form in (14) can account explicitly for bore deformation away from circular shape. In the final form, however, any such effect is forced into the Δ term.

We have now obtained a complete separation between capillary distortion and water compression-expansion effects. The Eq. (14) result can clearly be improved as follows. Let N_{00} be given by Eq. (10) with $R_b \rightarrow R_{b0}$ in (11)-(13). Then, to reinstate the r_p effect in Eq. (14), we need only write

$$N_0 \cong N_{00} + 2\int \Delta(r)\, dr. \tag{15}$$

The constituents of $N_{00} \equiv I_{10} + 2(I_{20} + I_{30})$ are

$$I_{10} = r_1 - \Omega^-[2r_1^3/3) - (R_{b0}^2 r_1/4)] - [b^-(\Omega^-)^2] \times [(8r_1^5/15) - (R_{b0}^2 r_1^3/3) + (R_{b0}^4 r_1/8)], \tag{16}$$

$$I_{20} = (r_2 - r_1) + \Omega^+[(r_2^3/3) - r_2 r_1^2 + (2r_1^3/3) + (R_{b0}^2/4) \times (r_2 - r_1)] - [b^+(\Omega^+)^2][(r_2^5/5) - (2r_2^3 r_1^2/3) + r_2 r_1^4 - (8r_1^5/15) + (R_{b0}^2/2)\{(r_2^3/3) - r_2 r_1^2 + (2r_1^3/3)\} + (R_{b0}^4/8)(r_2 - r_1)], \tag{17}$$

and

$$I_{30} = (\pi R_c/2)[1 + \Omega^+\{(r_2^2 - r_1^2) + (4r_2 R_c/\pi) + (R_c^2/2) + (3R_{b0}^2/8)\} - [b^+(\Omega^+)^2]\{(r_2^2 - r_1^2)^2 + \{8r_2 R_c(r_2^2 - r_1^2)/\pi\} + R_c^2(3r_2^2 - r_1^2) - (16r_2 R_c^3/3\pi) + (3R_c^4/8) + (R_{b0}/2)^2[(5r_2^2 - 3r_1^2) + (13R_c^2/4) - (8r_2 R_c/\pi)] + (41R_{b0}^4/192)\}]. \tag{18}$$

Although the R_{b0} terms in (16)-(18) are of no importance for the WC data and will be dropped hereafter, they have been included here to cover future situations where either R_{b0} is larger and/or the data are more precise.

C. Capillary Tube Deformation Corrections

To evaluate the integral in (15), first let $\Delta(r) \equiv \Delta_1(r) + \Delta_2(r) + \Delta_3(r)$. Here $\Delta_1(r)$ arises from the inside–outside pressure differential in water-filled regions; $\Delta_2(r)$ accounts for the relative change in R_b arising from stretching and compression of the straight parts of the tube containing water; and $\Delta_3(r)$ arises from distortion of the bent portion of the capillary from a circular to noncircular bore during rotation. Because we are dealing with sufficiently small strains that the theory of infinitesimal elasticity is a good approximation, linearity applies and the three Δ_i effects may be calculated independently.

Were the capillary tube unsupported at the ends, rapid rotation would lead to very appreciable tube stretching and consequent bore narrowing. Fortunately, however, the bent parts of the capillary are encased in rigid epoxy which abuts steel end caps in the aluminum rotor used (see Fig. 2 of Ref. 1). The only over-all stretching of the bottom part of the capillary then possible is that allowed by expansion of the rotor itself during rotation. Current measurements by a student of Winnick are under way to investigate the effect. It will be neglected here, although any appreciable over-all stretching could lead to a significant contribution to Δ of the same character as that of Δ_1, to be discussed below. Although zero net stretching still allows localized stretching and compression in the bottom leg, my colleague Dr. W. W. Boyd has shown that the resulting over-all volume change is zero to high order. He also finds that the area change of the bore at the center of the bend arising from the noncircular cross section of the bore under rotation is so small that Δ_3 may be neglected as well in the present context.

Remaining to be calculated are Δ_1 and the contribution to Δ_2 from rotational compression of the top part of the capillary between r_1 and r_2. Boyd has found that the latter effect leads to $\Delta_2 \cong \nu(r^2 - r_e^2)$, where $\nu \equiv \rho_p \omega^2 \sigma / 2E$ and ρ_p, σ, and E are the density, Poisson's ratio, and Young's modulus, respectively, of the Pyrex tube. The quantity r_e is defined in Fig. 1; its value is about 4 cm. Here ρ_p is taken independent of position, an adequate approximation in the present situation.

The well-known solution for the deformation of a hollow cylindrical tube with pressure P_a outside and P_i inside may be used to calculate Δ_1. For a thick-walled tube, the result may be expressed as

$$\Delta_1 = (K_0 z/E)(1 + \sigma\{[(R_0/R_{b0})^2 + 1]/[(R_0/R_{b0})^2 - 1]\}), \equiv \xi K_0 z \equiv \alpha z, \tag{19}$$

where z is given by Eq. (5), K_0 is the bulk modulus of water, and $2R_0$ is the outer diameter of the tube. Note that P_a has canceled out of this expression. R_0/R_{b0} is about 7 for Tubes 51 and 58 and about 10 for Tube 7.[4] The term multiplying σ varies from about 1.04 to about 1.02, and thus Δ_1 depends only slightly on (R_0/R_{b0}).

We may now write

$$N_0 - N_{00} \cong 2\alpha \int z\, dr + 2\nu \int_{r_1}^{r_2} (r^2 - r_e^2)\, dr. \tag{20}$$

The quantity multiplying 2ν in (20) is about 50 cm^3 for Tube 58. On using[13] $\rho_g = 2.3$ g/cm^3, $\sigma = 0.24$, and $E = 6.2 \times 10^{11}$ dyn/cm^2, one finds for $\omega = \omega_m$ that $\nu = \nu_m \simeq 1.6 \times 10^{-6}$ cm^{-2}. Thus, the Δ_2 term in Eq. (20) contributes at most about 1.6×10^{-4} cm. This is comparable in magnitude to other errors discussed and neglected by WC and is small compared to the sizes of the remaining terms in N_0. Thus, it will be neglected for simplicity here although it and possibly even the small Δ_3 contribution should be included in a precise treatment of good data.

When Eq. (20) is evaluated and the result combined

TABLE III. Results of least squares fitting of Winnick and Cho 20°C data.

Line	Fitting method tube	Data	Deformation correction	s_d (cm)	Parameter estimates $\hat{K}_0$ (bar)	$\hat{K}_0'$
1	I-58	S–U	No	1.64×10^{-5}	13 238±25	5.91±0.68
2	I-58	S–U	No	1.64×10^{-5}	13 284±25	6.03±0.69
3	I-58	S–C	No	7.56×10^{-6}	22 965±35	4.81±0.93
4	I-58	U–C	No	4.75×10^{-5}	22 977±219	5.1±5.8
5	I-7	U–C	No	8.96×10^{-5}	22 729±443	−11.8±11.4
6	I-51	U–C	No	3.65×10^{-5}	22 724±183	−2.4±4.7
7	I-58	U–C	Yes	4.75×10^{-5}	24 459±248	6.0±6.6
8	I-7	U–C	Yes	8.96×10^{-5}	24 164±501	−13.2±12.9
9	I-51	U–C	Yes	3.65×10^{-5}	24 114±206	−2.5±5.4
10	II-58	U–C	Yes	4.75×10^{-5}	26 149±432	6.0±6.3
11	II-7	U–C	Yes	8.96×10^{-5}	25 663±866	−11.8±11.6
12	II-51	U–C	Yes	3.65×10^{-5}	25 730±372	−1.8±4.9
13	II-58	U–C	Yes	4.60×10^{-5}	25 880±51	···
14	I-58	U–C	Yes	4.61×10^{-5}	24 282±29	···
15	III-58	U–C	Yes	4.65×10^{-5}	16 877±40	···

with that for N_{00}, one finds that the remaining tube deformation correction leads to the replacement in (16)–(18) of $\Omega^\pm$ by $(1+2\alpha)\Omega^\pm$ and $b^\pm(\Omega^\pm)^2$ by $(b^\pm-\alpha)(\Omega^\pm)^2$. These corrections are small but not negligible. For Tube 58, e.g., $\alpha\simeq0.044$, using $K_0=2.18\times10^4$ bar and the above Pyrex material parameters.

D. The $\Delta r(W)$ Equation

The result of setting $(N_0)_\omega=(N_0)_{\omega=\omega_m}$ may be written

$$\Delta r(W)=(QW-Q_mW_m)+(R_mW_m^2-RW^2), \quad (21)$$

where $W\equiv(K_0^\pm)^{-1}\Omega^\pm\equiv(\rho_0/2)\omega^2$,

$$Q\equiv[(2r_2^3/3)-2r_2r_1^2+(4r_1^3/3)+\pi R_c(r_2^2-r_1^2)+4r_2R_c^2+(\pi R_c^3/2)]C^+-(2r_1^3/3)C^-, \quad (22)$$

$$R\equiv[(-16r_1^5/15)+(2r_2^5/5)+2r_2r_1^4-(4r_2^3r_1^2/3)+\pi R_c(r_2^2-r_1^2)+8r_2R_c^2(r_2^2-r_1^2)+\pi R_c^3(3r_2^2-r_1^2)-(16r_2R_c^4/3)+(3\pi R_c^5/8)]D^++(8r_1^5/15)D^-. \quad (23)$$

In these equations

$$C^\pm\equiv(1+2\alpha)(K_0^\pm)^{-1}=[(K_0^\pm)^{-1}+2\xi], \quad (24)$$

$$D^\pm\equiv(b^\pm-\alpha)(K_0^\pm)^{-2}=[\{(K_0'^\pm-2)/2\}-K_0^\pm\xi]\times(K_0^\pm)^{-2}. \quad (25)$$

It is thus $C^\pm$ and $D^\pm$ which involve the $K_0^\pm$ and $K_0'^\pm$ free or fixed parameters which apply in the positive and negative pressure regions.

Since Eq. (21) cannot be readily solved for Δr explicitly, and since $\Delta r\ll r_1$, simplification is desirable and possible. Expand Q and R in Taylor series around $r_1=r_{1m}$ up to terms in Δr only. Although it may easily be shown that $(\Delta r)^2$ and higher terms are negligible for the present data precision, $(\Delta r)^2$ terms should be retained for more precise data, especially that for more compressive liquids or larger negative pressures, where Δr_m is larger. The result is

$$\Delta r(W)\cong[Q_m(W-W_m)+R_m(W_m^2-W^2)]/[1-Q_m'W+R_m'W^2], \quad (26)$$

where

$$Q_m'=2r_{1m}[2(r_{1m}-r_2)-\pi R_c]C^+-2r_{1m}^2C^-, \quad (27)$$

$$R_m'=[(-8r_{1m}/3)\{2r_{1m}^3-3r_2r_{1m}^2+r_2^3\}-(2r_{1m}R_c)\{2\pi(r_2^2-r_{1m}^2)+8r_2R_c+\pi R_c^2\}]D^++(8r_{1m}^4/3)D^-. \quad (28)$$

Equation (26) is the final fitting equation; note that it involves the equation of state parameters nonlinearly. For typical values of the quantities appearing in Eq. (22) and $r_1=r_{1m}$, $Q_m\cong60C^+-180C^-$; thus, Q_m will be negative and the dominant term in (26), $Q_m(W-W_m)$ will always be positive as it should be.

IV. DATA FITTING RESULTS

A. Published Data

The first three lines of Table III show the results of least squares fitting of Eq. (26) to the Tube 58 published WC data using the values given in Table II. Here I designates the case where K_0^- and $K_0'^-$ are free and K_0^+ and $K_0'^+$ are fixed, that used by WC. Case II is that where the same free K_0 and K_0' parameters are used in both negative and positive regions and

Case III is the reverse of I. S–U denotes smoothed, uncorrected data and U–C unsmoothed, corrected data.

Line 1 is the situation analyzed by WC. They used the fixed input values $B^+=2790.4$ bar and $K^+=0.13041$. On taking $V_0=1.001840$, $P_0=0.0234$ bar, $K_0=(K_0'+1)(B+P_0)$, and $K_0'=(V_0/K)-1$, I find these values correspond to $K_0^+\cong 21\,437$ bar and $K_0'^+\cong 6.6822$. These are the fixed values used in the line 1 fitting. Since it has been established earlier that the values $K_0^+\cong 21\,796$ bar and $K_0'^+=5.20$ are considerably more appropriate, however, they are used in all succeeding Case I and III fittings. Incidentally, to ensure the least squares character of these nonlinear fittings, all results were checked against the results of fitting with an approximate form of (26) where the parameters entered linearly.

Although the difference between the results of lines 1 and 2 is not significant, the $\hat{K}_0^-$ values obtained are nearly a factor of 2 too small! When WC were apprised of the result (which also appears for Case II fittings), they discovered that an instrumental magnification factor of 2.165 (not mentioned in WC or in Cho's thesis) had not been applied to the published data, that appearing in Table III of the WC paper. All lengths in this table are thus too large by this factor, but it apparently did not affect WC's own parameter estimation results.

Correction of the WC data by the 2.165 factor and fitting as in line 3 leads to a much more likely value of $\hat{K}_0^-$. Incidentally, these $\hat{K}_0^-$ and $\hat{K}_0'^-$ values correspond to $\hat{B}^-\cong 3953$ bar and $\hat{K}^-\cong 0.172$ cm^3/g. For comparison, WC found $\hat{B}^-=2878.8$ bar and $\hat{K}^-=0.12550$ cm^3/g for this tube. The large differences apparent may largely arise from WC's approximate fitting formula and from their likely failure to achieve a true least squares solution. On the other hand, their values lead to $\hat{K}_0^-\cong 22\,981$ bar, very close to the line 3 K_0^- value, and their parameter estimates do, in fact, lead to a reasonable representation of the data within the expected experimental accuracy. Had they actually calculated such a $\hat{K}_0^-$ value, they might well have concluded that the experiment yielded satisfactory results, at least for this parameter. But, as we shall see, one must not stop the analysis here.

Private communication with WC next made it clear that their data were smoothed. Since all present fittings of these data led to highly correlated residuals, showing large systematic error, it became clearly desirable to use the unsmoothed thesis data[4] for further fitting. Such data naturally lead to higher standard deviations, but the residuals obtained generally showed little or no correlated systematic behavior and were normally distributed to good approximation. Thus, the parameter estimates and standard deviations obtained from the unsmoothed data may be trusted much more than those obtained from the smoothed data.

Because there are random errors in both W and Δr values, generalized least squares should be used for fitting these data.[8,9,11] Since there is, unfortunately, insufficient information in WC[1,4] to yield trustworthy weightings for individual W and r_1 values, all the present fittings have been carried out using ordinary nonlinear least squares, which involves unity weighting of Δr and the assumption of no random errors in W.

B. Thesis Data[4]

The line 4–15 results have been obtained using corrected, unsmoothed data.[4] Results are first shown for the three different tubes analyzed by WC. Note the greater uncertainty of the line 4 results compared to those of line 3 for smoothed data. Clearly, no unsmoothed data fittings lead to $\hat{K}_0'$ values of any significance whatsoever. Comparison of line 4–6 results with the corresponding line 7–9 results shows that the deformation correction leads to about a six per cent change in $\hat{K}_0^-$ values. Unfortunately, it moves $\hat{K}_0^-$ away from the expected value of 21 796 bar; line 7–9 $\hat{K}_0^-$ values are about 11% larger than this value.

Next, lines 10–12 show the results of Case II fitting. Values of $\hat{K}_0$ are about 6.5% larger than the corresponding Case I results and about 18% larger than 21 796 bar. Further, the Case II tube deformation correction leads to a larger change in $\hat{K}_0$ than for Case I. Fitting results not listed in the table show that the inclusion of this correction leads to somewhat more than a 10% increase in K_0 values for these three tubes.

Since K_0' estimates are without significance here, K_0 estimation should be improved by eliminating K_0' entirely as a free parameter. This can be done by fixing K_0' at zero, but for the present data a slightly better fit is obtained by eliminating all second order effects through setting $R_m=R_m'=0$ in Eq. (26). Lines 13–15 show representative Tube-58 fitting results for this condition for Cases II, I, and III. As expected, the estimated standard deviations of the $\hat{K}_0$ values are much smaller when K_0 is the only parameter determined. Thus, the differences in $\hat{K}_0$ values from 21 796 bar for the various cases appear to be highly significant. Results for the other tubes are similar, and the inclusion of the tube deformation correction again leads to the same percentage increases as above.

C. Conclusions

Case II results are probably more significant than those of I and III. In these latter cases, $\hat{K}_0^\mp$ output values are partly determined by the fixed $K_0^\pm$ input values used. Note nevertheless that the Case III result for $\hat{K}_0^+$ indicates the same sort of anomaly in $\hat{K}_0$ as those evident for Cases I and II. None of these results shows unambiguously, however, that the anomalies arise only from the behavior of water in the negative pressure region.

It is unfortunate that meaningful estimates of K_0' cannot be obtained from the WC data because if there should be any significant difference in the behavior of water under positive and negative pressures near zero, one would expect it to show up more importantly in K_0' than in K_0. To establish any such effect, one would require either more precise data and/or larger negative pressures.

On the other hand, the line 7–15 results for $\hat{K}_0$ show large and significant differences from the expected value of 21 796 bar. These differences may arise from three causes: (a) systematic errors in the data analyzed; (b) an inadequate theory of the experiment; and (c) a very considerable difference in the response of water to positive and negative pressures of less than 75 bar. WC carried out their original experiments to test whether liquids under negative pressure follow the same equation of state as those under positive pressure.[1] This suggests that in this low-pressure region they believed that there might indeed be a measurable difference. Since there is every reason to expect that one can expand the density in a Taylor series around $p=0$, as in Eq. (2), it seems exceedingly implausible that appreciably different values of K_0 might be required for the regions -75 bar$<p<0$ bar and 0 bar$<p<75$ bar. Certainly if p were sufficiently negative to bring the water near the cavitation region, one would expect that the usual quadratic dependence on separation of the intermolecular force between molecules would fail, but the present experiment comes nowhere near this region. Thus, although neither possibility (b) nor (c) can be absolutely ruled out, I believe that (a) is the most likely explanation for the present discrepancies.

Finally, it is clear that tube deformation during rotation contributes significantly to Δr and should not be neglected in an adequate account of the present type of experiment. Since it exhibits exactly the same dependence on ω that water deformation itself shows, within the limits of applicability of linear elasticity theory for the capillary tube, the two effects cannot be readily separated or changed in relative importance by changing ω. On the other hand, tube deformation will be of less relative importance for a liquid more compressible than water.

In conclusion, it appears that (a) sources of systematic error likely to be present in the WC data should be isolated and controlled; (b) measurements of Δr, r_{1m}, and ω values should be refined and replicated enough to establish their individual uncertainties; and (c) improved data should then be analyzed by the present theory, using generalized least squares. The results should allow reasonably reliable values for K_0 and possibly even K_0' to be obtained, but, unless ω_{max} and/or r_{1m} can be so increased that the maximum tensile strength of water can be approached much closer than it has been so far in this kind of experiment, it seems unlikely to me that important new physical insights into the behavior of water under negative pressure may be expected from the experiment. Further, since the tube deformation correction is an appreciable part of the total contribution to Δr, small uncertainties in the elastic properties of the pyrex actually used in an experiment, and perhaps even in the form of parts of the correction itself, will make it difficult either to derive very accurate values of K_0 and K_0' from this kind of an experiment or to achieve meaningful discrimination between various different equations of state for the negative pressure region.

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APPENDIX: EQUATIONS OF STATE CONSIDERED

A. Definitions

At $P=P_0$, $V=V_0$. Let $p\equiv P-P_0$ and $w\equiv(V_0-V)/V$

B. Tait Equation

$$V-V_0=-C\log_{10}[(B+P)/(B+P_0)]$$
$$\equiv -K\ln[(B+P)/(B+P_0)]$$
$$(V/V_0)=1-(K_0'+1)^{-1}\ln[1+(K_0'+1)(p/K_0)]$$

C. 3DGE

Nonlinear form:

$$p=K_0[w+[\tfrac{1}{2}(K_0'-1)]w^2+\tfrac{1}{6}(K_0'^2-3K_0'+2+\psi)w^3]$$

Linear form:

$$p=\sum_{i=0}^{3}A_iw^i$$

D. 2DGE

$$p=K_0[w+\tfrac{1}{2}(K_0'-1)w^2]$$

E. VQE

$$(V/V_0)=1-(p/K_0)+\tfrac{1}{2}(K_0'+1)(p/K_0)^2$$

F. DQE

$$(\rho/\rho_0)=(V_0/V)=1+(p/K_0)-\tfrac{1}{2}(K_0'-1)(p/K_0)^2$$

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Ozone Ultraviolet Photolysis. V. Energy Distribution in the $O(^1D)+O_3$ Reaction*

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The experiments described in this paper concern the distribution of vibrationally excited $O_2^\dagger$ following flash photolysis of ozone under conditions which permit an improved extrapolation to find the distribution in which they are initially formed. The observed states $v''=14$–21 are found to have an initial distribution which can reasonably be described by a vibrational temperature, $T_{vib}=23\,400\pm1260$°K. The origin of the distribution and the proportionation of product between $2O_2^\dagger$ and $2O(^3P)+O_2$ is discussed in terms of a statistical model. This interpretation accounts for the observed distribution of $O_2^i(i=14$–$21)$, it accounts for the predominance of $2O(^3P)+O_2$ product in gas phase photolysis, and for the predominance of $2O_2$ products in photolysis of liquid Ar solutions. An inert gas pressure dependence of the reaction product distribution is predicted and observed qualitatively.

I. INTRODUCTION

The $O(^1D)+O_3$ is the most energetic of the various A+BCD reactions which have been studied,[1–3] producing vibrationally excited $O_2^\dagger$ which has been observed[4] in states as high as $v''=30$. The purpose of this research is to determine the distribution in which this $O_2^\dagger$ is initially formed. The experiment is flash photolysis of an ozone–argon mixture accompanied by photoelectric absorbance measurements at wavelengths of selected rotation–vibration lines of the levels accessible to measurements in the Schumann–Runge system. The reaction sequence to be considered is

$$O_3+h\nu\rightarrow O(^1D)+O_2(^1\Delta), \quad (1)$$

$$O(^1D)+O_3\rightarrow 2O_2^\dagger, \quad (2a)$$

$$O(^1D)+O_3\rightarrow 2O(^3P)+O_2, \quad (2b)$$

$$O(^1D)+Ar\rightarrow O(^3P)+M, \quad (3)$$

$$O_2^i+O(^3P)\rightarrow O_2^j+O(^3P). \quad (4)$$

Part III of this series,[4] showed that formation of $O_2^\dagger$ by reaction (2a) is a minor reaction path and identified the major path (2b) as one forming $2O(^3P)$. [*Note added in proof:* This $O(^3P)$ has also recently been observed directly by resonance fluorescence (R. P. Wayne, private communication).] The literature pertinent to the other processes is referenced in that paper. Part IV then showed[5] that relaxation of the $O_2^\dagger$ occurs largely by collisions with $O(^3P)$ when the $[O(^3P)]/[O_3]$ concentration ratio is not too small. Reaction (4) is a matrix of processes which can be represented by rate constants

$$k_{ij}=6\times10^8[1+0.04(i-1)]$$

with $i>j$ under the conditions to be studied.

All known reactions of this system other than those which are given are too slow to contribute significantly on the time scale of the present experiments. At higher temperatures the reaction

$$O_3+O(^3P)\rightarrow 2O_2^\dagger \quad (5)$$

is fast enough to produce a significant amount of $O_2^\dagger$. It is now clear that the distribution observed in the earlier work by Fitzsimmons and Bair[6] resulted from some unresolved combination of Reactions (2a) and (5). The present research takes advantage of subsequent information and technology to study the distribution of $O_2^\dagger$ from (2a) alone.

II. EXPERIMENTAL RESULTS

The details of the experimental system and procedures for measuring the data and reducing it to population distributions have been adequately described previously.[5,6] The primary data of the experiment are illustrated by the data points in Fig. 1. Part IV treated the data at time $t\geq40$ μsec to obtain a system of relaxation rate constants. In the present work these constants are used to calculate distribution constants, f_i, the fraction of Reaction (2) that is (2a)+(2b), which produces vibrationally excited O_2^i initially in vibrational level i. This is done by numerical integration of the rate expression for Reactions (1), (2a), (2b), (3), and (4), using previously measured