

HIGH TEMPERATURE SOLUBILITY OF SULFUR DIOXIDE
IN CONCENTRATED SULFURIC ACID

by

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INTRODUCTION

In the course of a study of the kinetics of the isotopic exchange reaction between sulfur dioxide and concentrated sulfuric acid it became necessary to have data on the high temperature solubility of the gas in the acid. A review of the literature failed to yield the desired information.

Miles and Carson (7, pp.786-790), who included the results of earlier workers, while covering the desired range of acid concentration, did not work at a higher temperature than sixty degrees centigrade, while the need was for solubility data in the vicinity of two hundred degrees centigrade. Milbauer (6, pp.221-224), though working up to a temperature of two hundred and thirty-seven degrees centigrade, obtained results for an acid concentration of ninety and eight-tenths percent only; the need in the present instance was primarily for acid concentrations higher than this.

In view of the above, it became necessary to determine the missing data: specifically, the sulfur dioxide solubility in a sulfuric acid concentration range of eighty-five to ninety-eight percent, and in a temperature range of one hundred and sixty to two hundred and twenty-five degrees centigrade.

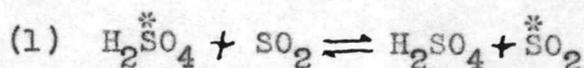
The method of determination used involved a direct application of knowledge previously gained about the sulfur dioxide-sulfuric acid exchange reaction. It has been shown that the rate is (a) proportional to the gas pressure and (b) proportional to the volume of sulfuric acid present.^a The interpretation of these two observations is that the rate depends on the amount of gas dissolved in the acid. This conclusion suggested a method of solubility determination: by progressively decreasing the gas space over the acid, the rate should increase, approaching a maximum for zero gas space. Analysis of the data thus obtained should make possible calculation of the gas solubility.

This thesis, therefore, not only concerns itself with solubility determination of sulfur dioxide in sulfuric acid, but it also is an attempt to show a unique method for this particular determination. Further applications of this technique to problems other than the one concerned here have not been considered, but it is safe to presume that such applications might exist.

^a Norris, T. H. and B. J. Masters. Kinetics of Isotopic Exchange Reaction between Sulfur Dioxide and Concentrated Sulfuric Acid. Chemistry Department. Oregon State College. 1952. To be published.

THEORY

The exchange reaction under consideration may be written as follows:



Duffield and Calvin (1, p.599) have shown that for such a reaction the rate of exchange R is given by

$$(2) \quad R = \frac{-2.3}{t} \frac{ab}{a+b} \log (1-F)$$

where, in our case, a is equal to the amount of sulfur dioxide, and b is equal to the amount of sulfuric acid. F is the fraction of exchange equilibrium at time t.

The progress of the exchange is followed by measuring the increase in activity of the sulfur dioxide. Norris (9, p.779) states that F may be calculated from specific activities of the reactants as follows:

$$(3) \quad F = \frac{\text{Specific activity of gas at time } t}{\text{Spec. act. of gas at infinite time}} = \frac{x}{x_{\infty}}$$

The quantity in the numerator of the above equation can be directly measured while the quantity in the denominator is determined indirectly as follows:

$$(4) \quad x_{\infty} = \frac{(\text{Spec. act. of acid at } t=0) (\text{Amt. of acid})}{(\text{Amount of gas} + \text{acid})}$$

As mentioned in the previous section, it has been found that the rate of the exchange reaction varies with

the amount of acid and with the pressure of the gas. From this earlier work, then an attempt was made to calculate a rate constant as follows:

$$(5) \quad R = k' \frac{(\text{amount of gas}) (\text{volume of acid})}{(\text{total volume of gas + acid})}$$

where, for large gas volume, the amount of gas divided by the total volume of gas plus acid is approximately proportional to the pressure of the gas, and the volume of the acid is proportional to the amount of the acid. The volume of acid divided by the total volume of gas plus acid will henceforth be called R' . Equation (5) now becomes

$$(6) \quad R = k' (\text{amount of gas}) R'$$

The rate constant as calculated from (6), however, is not a true rate constant, since it rests on the assumption of an inverse proportionality between sulfur dioxide pressure and total volume (gas plus acid); an assumption only approximately valid, and decreasingly so as the gas volume grows smaller and comparable to the acid volume. In other words, k' is itself a function of R' .

A new rate expression is now, then, assumed:

$$(7) \quad R = k (\text{amount of gas}) F'$$

where k is a true rate constant and F' is the fraction of total gas dissolved in the acid.

On the basis of the relatively low solubilities involved at these high temperatures, it is assumed that

Henry's Law is obeyed and that one may define a distribution coefficient, c . On this basis it is possible to derive the following relationship between F' , R' and c :

$$(8) \quad c = \frac{SO_{2a}/Vol_a}{SO_{2g}/Vol_g} \quad (\text{defines } c)$$

$$(9) \quad 1 + \frac{SO_{2g}}{SO_{2a}} = \frac{Vol_g}{Vol_a c} + 1$$

$$(10) \quad \frac{SO_{2a} + SO_{2g}}{SO_{2a}} = \frac{Vol_g + Vol_a c}{Vol_a c} = \frac{1}{F'}$$

$$(11) \quad F' = \frac{c Vol_a}{Vol_g + Vol_a c} = \frac{c Vol_a}{Vol_{tot} - Vol_a + c Vol_a}$$

$$= \frac{c Vol_a}{Vol_{tot}} = \frac{c R'}{1 - R' + c R'}$$

$$= \frac{1 - \frac{Vol_a}{Vol_{tot}} + c \frac{Vol_a}{Vol_{tot}}}{1 - R' + c R'}$$

Now by equating equation (6) to equation (7) one gets

$$(12) \quad k' (\text{amount of gas})R' = k (\text{amount of gas})F'$$

which upon cancellation and substitution becomes

$$(13) \quad k' = k \frac{c}{1 - R' + c R'}$$

Taking the reciprocal of (13) and factoring where necessary,

the desired final equation is obtained:

$$(14) \frac{1}{k'} = \frac{1}{kc} [1 + (c-1) R']$$

As can be seen from equation (14), a plot of $1/k'$ versus R' should yield a straight line whose intercept at $R'=0$ gives $1/k' = 1/kc$. The intercept at $R'=1$ gives $1/k$. From these values, then, the intercept at $R'=1$ divided by the intercept at $R'=0$ yields the quantity, c .

A method for determining the solubility of sulfur dioxide in sulfuric acid in terms of the distribution coefficient, c , can now be set up. The general technique for a given acid concentration and temperature is to hold the quantities of acid and gas fairly constant, and vary the size of the bomb in which the reaction is carried out. For each run, then, a rate is calculated by equation (2), and $1/k'$ is calculated from equation (6). A plot of the $1/k'$ values versus R' should give the desired straight line from whose intercepts c may be computed.

EXPERIMENTAL PROCEDURES

The sulfur dioxide was obtained from a commercial cylinder. Two washings with concentrated sulfuric acid and drying over phosphorus pentoxide preceded the condensation into a vacuum system. Fractional distillation of the liquid in vacuum, the middle fraction being saved, completed the purification steps.

The sulfuric acid was c.p. grade reagent, which was distilled; the middle fraction saved for use as the stock supply. From time to time the acid was titrated with standard base and found always to be 98.0 percent (plus or minus 0.1 percent) hydrogen sulfate. All other concentrations of acid were prepared from this stock supply by weight dilutions with distilled water to within an accuracy of one-tenth of a percent unit. All handlings of the acids were conducted in a moisture free atmosphere as obtained in a dry box. Portions of the stock acid were activated from time to time with the eighty-seven day half-life radioisotope, sulfur thirty-five, according to the procedures of Masters and Norris (5, p.2395).

The actual procedures throughout utilized all glassware and standard high vacuum techniques. Gas transfer was accomplished by vacuum distillations with the aid of liquid nitrogen. The bombs in which the exchanges were run

consisted of two main types: either (a) what may be called a test tube type or (b) a capillary type.

The test tube type bomb, for volumes of approximately twenty, ten and one milliliter, were fitted with a side arm for filling purposes. The end of the side arm was a ground glass joint for attachment to the vacuum line. The tube part of the bombs was made from tubing whose outside diameter was sixteen millimeters for the twenty milliliter bomb, fourteen millimeters for the ten milliliter bomb, and six millimeters for the one milliliter bomb. The top of the bomb was fitted with a break-off tip. The volumes were determined by filling with a liquid (water usually, or acetone for the small bombs) from a microburette.

The capillary type bomb, for volumes less than one milliliter, consisted of a capillary tube (approximately two millimeters inside diameter) sealed at one end. The other end was fitted with a ground glass joint for filling and attachment to the vacuum line. The volumes were determined by filling with a weighed amount of liquid of known density (usually the acid itself).

The filling procedure for both types of bomb was the same. In a dry box, an approximately known amount of acid was pipetted into the weighed empty bomb. An additional weighing of the bomb determined the amount of acid contained therein. The bomb was then attached to the vacuum

line and evacuated. From a dosing bulb of known volume filled with sulfur dioxide at a known temperature and pressure, the gas was frozen into the bomb which was then sealed off from the vacuum line.

The bombs were immersed in a well regulated (plus or minus one-tenth of a degree centigrade) oil thermostat for various lengths of time. The regulator of the bath was set for the different temperatures from time to time. It had previously been shown^b that the rate of exchange is proportional to the amount of acid and that the diffusion rate is not a limiting factor; nevertheless, the bombs were placed on their sides in the thermostat and agitated in order to insure maximum acid surface exposure to the gas.

Considerable difficulty was encountered from the capillary bombs' exploding at these high temperatures, due to the internal pressure exerted by the gas. Extreme care had to be exercised in the making, sealing and annealing of the bombs in order to assure the strongest of structures; even so, no data could be obtained for the capillary bombs run at the highest temperature (225.3 degrees centigrade) that was attempted, due to this problem.

At this point it might well be noted that the half-time of the exchange at room temperature is of such length,

^b Norris, T. H. and B. J. Masters. Kinetics of Isotopic Exchange Reaction between Sulfur Dioxide and Concentrated Sulfuric Acid. Chemistry Department. Oregon State College. 1952. To be published.

that, for all practical purposes, no exchange takes place during the lost time between filling the bombs and the actual high temperature run, and between the high temperature run and the opening of the bombs to recover the sulfur dioxide. This convenient fact made possible the preparation of bombs in batches prior to the time at which they were to be run.

The sulfur dioxide was recovered from the test tube type bombs by attaching the break-off tip end of the bomb, containing a magnetic breaker, to the vacuum line by means of a ground glass joint. Also attached to the vacuum line was an absorption bomb containing a frozen sodium hydroxide solution. The entire system was evacuated and the break-off tip broken by the breaker; the sulfur dioxide was then frozen into the absorption bomb, which was finally sealed off from the vacuum line.

The opening of the capillary bombs necessitated the construction of a separate glass apparatus for each bomb. The apparatus was in the shape of an elongated and inverted T made from fifteen millimeter outside diameter tubing. The bomb, heavily scratched around the middle, was sealed into the cross member, the two ends being supported above the bottom of the tube by means of indentations in this tube. The foot of the T, containing a steel ball, was attached to the vacuum line by means of a ground glass

joint and the apparatus was evacuated. The steel ball was raised about sixty centimeters by means of a magnet and allowed to drop upon the exposed and unsupported part of the bomb, thus breaking it in half. The sulfur dioxide was then frozen into an absorption tube as in the case of the test tube type bomb.

All samples, either sulfur dioxide or sulfuric acid where necessary, were converted to barium sulfate for purposes of radioassay. Following standard procedures of Norris (9, pp.1220-1223), these samples were mounted on nickel-plated planchets for counting under an end-window Geiger-Muller counter tube, self-absorption, coincidence and decay corrections being applied as necessary.

Since the calculation of the results required a knowledge of the acid volumes, it was necessary to have values of the acid densities. These data are not available in the literature for the high temperatures involved in this work; however, since no radioisotope work can yet pretend to the highest precision, sufficiently good estimates were obtained by extrapolation to higher temperatures of the data appearing in International Critical Tables (10, pp.56-57).

As a further approximation, no allowance was made for the effect on the volume of dissolved sulfur dioxide. Although this was not always insignificant, trial calculations.

showed that its neglect had but little effect on the solubilities eventually calculated. The extrapolated densities used are summarized in Table I.

TABLE I

ACID DENSITIES

<u>% Acid</u>	<u>Temp.-°C.</u>	<u>Density</u>
98.0	194.4	1.673
98.0	167.5	1.698
98.0	181.4	1.685
98.0	225.3	1.646
90.8	225.3	1.619
90.8	194.4	1.648
90.8	167.5	1.673
97.0	194.4	1.674
96.0	194.4	1.671
94.9	194.4	1.668
93.1	194.4	1.662
85.2	194.4	1.608

RESULTS

The experimental results are summarized in Table II. Each run represented an individual bomb. The fractional exchange values shown were calculated in the manner discussed in Section II. As a check on the experimental procedure, the data from each of the four sets of bombs with 98.0 percent acid at 194.4 degrees centigrade were plotted as $\log (1-F)$ versus time. In all cases good straight lines were obtained in conformity to the requirement that an isotopic exchange must follow a first order rate law (cf. equation 2).

From the quantities appearing in Table II a rate was calculated for each run by equation (2) and $1/k'$ by equation (6). These two values along with R' appear in Table III.

For each acid concentration at the different temperatures the $1/k'$ and R' values that appear in Table III were averaged for the runs representing approximately the same volumes. These points were plotted as $1/k'$ versus R' and straight lines were drawn through the results as shown in Figures 1 through 5. As discussed in Section II the ratio of the intercepts of the straight lines obtained in plots of this type yields the distribution coefficient, c . These c values are summarized in Table IV.

TABLE II
EXPERIMENTAL RESULTS

Run #	Milli- moles gas	Milli- moles acid	Acid moles cc.	Bomb vol., cc.	Exch. time, hrs.	Spec. act. ^e of gas	F
98.0 % acid at 194.4° C.							
6	0.332	9.02	0.540	1.16	10.0	604 ^a	0.519
7	0.334	8.33	0.499	1.20	2.0	157	0.135
8	0.332	8.26	0.494	1.18	4.0	261	0.225
10	0.332	8.79	0.526	1.24	8.0	456	0.392
11	0.332	8.44	0.505	1.22	12.0	555	0.494
12	0.332	8.91	0.533	2.00	3.0	145	0.124
13	0.325	9.22	0.551	2.00	6.0	293	0.251
14	0.328	8.69	0.520	1.98	9.0	346	0.297
15	0.330	9.14	0.547	2.00	11.47	465	0.399
16	0.331	8.69	0.520	2.18	15.0	531	0.456
19	0.326	9.99	0.600	0.647	6.0	472	0.403
20	0.331	9.25	0.554	0.596	3.08	280	0.240
21	0.331	9.25	0.554	0.569	9.0	682	0.584
22	0.337	9.48	0.567	23.2	30.0	225	0.193
23	0.333	9.48	0.567	24.0	50.0	297	0.255
24	0.333	9.48	0.567	23.8	71.0	399	0.342
98.0 % acid at 167.5° C.							
66	0.319	9.91	0.584	10.30	50.0	54 ^b	0.125
67	0.318	10.33	0.609	10.65	100.4	96	0.223
68	0.324	9.70	0.572	1.45	11.02	58	0.133
69	0.320	8.32	0.490	1.30	19.65	92	0.214
70	0.324	9.44	0.556	0.626	9.17	69	0.160
71	0.324	9.62	0.567	0.683	12.38	84	0.196
98.0 % acid at 181.4° C.							
86	0.320	10.3	0.611	0.730	8.0	141 ^b	0.327
94	0.322	9.29	0.552	10.00	49.25	117	0.271
95	0.318	9.53	0.566	10.25	42.4	100	0.231
96	0.321	9.26	0.550	1.20	19.7	202	0.467
97	0.321	8.50	0.508	0.594	2.5	45	0.105

Table II Continued

Run #	Milli- moles gas	Milli- moles acid	Acid vol., cc.	Bomb vol., cc.	Exch. time, hrs.	Spec. act.e of gas	F
98.0 % acid at 225.3° C.							
82	0.318	9.85	0.599	10.35	2.5	69 ^b	0.161
83	0.322	9.68	0.589	10.55	3.67	99	0.230
84	0.321	7.96	0.484	1.26	0.75	104	0.243
85	0.324	7.94	0.483	1.26	1.0	141	0.329
90.8 % acid at 225.3° C.							
88	0.318	8.77	0.585	9.85	2.5	100 ^b	0.232
89	0.318	8.47	0.565	9.75	3.67	137	0.319
90	0.318	7.66	0.512	1.10	0.75	173	0.405
91	0.319	7.59	0.506	1.10	1.0	206	0.481
90.8 % acid at 194.4° C.							
26	0.335	7.72	0.506	11.00	41.0	508 ^a	0.438
27	0.330	7.72	0.506	10.75	30.0	398	0.344
32	0.324	7.88	0.516	0.613	4.0	584	0.502
33	0.331	7.10	0.466	1.20	6.0	474	0.411
34	0.333	6.95	0.456	1.18	9.0	704	0.610
35	0.333	7.01	0.460	0.545	2.25	350	0.303
90.8 % acid at 167.5° C.							
72	0.319	8.70	0.562	10.75	50.0	65 ^b	0.150
73	0.318	8.44	0.545	10.70	100.4	114	0.264
75	0.323	7.15	0.462	1.40	50.4	237	0.556
76	0.321	8.45	0.545	0.652	24.27	212	0.494
77	0.321	9.44	0.610	0.682	19.32	191	0.444
97.0 % acid at 194.4° C.							
36	0.322	8.22	0.496	10.80	10.0	118 ^c	0.115
37	0.319	8.36	0.505	10.95	20.0	211	0.205
38	0.321	8.00	0.483	1.20	3.0	199	0.194
39	0.319	7.79	0.471	1.20	5.0	305	0.298
40	0.321	8.86	0.535	0.589	2.0	206	0.200
41	0.317	8.95	0.540	0.576	4.1	367	0.357

Table II Continued

Run #	Milli- moles gas	Milli- moles acid	Acid vol., cc.	Bomb vol., cc.	Exch. time, hrs.	Spec. act. ^e of gas	F
96.0 % acid at 194.4° C.							
42	0.327	9.14	0.558	10.75	10.0	142 ^c	0.138
43	0.324	8.35	0.511	10.70	20.0	243	0.237
45	0.321	7.68	0.470	1.26	5.0	325	0.317
47	0.321	10.27	0.628	0.735	2.0	220	0.213
94.9 % acid at 194.4° C.							
48	0.319	8.37	0.507	10.55	10.0	138 ^c	0.134
49	0.322	8.45	0.523	10.50	20.0	267	0.260
50	0.322	7.68	0.476	1.20	3.0	245	0.239
51	0.321	7.56	0.468	1.20	5.0	339	0.333
52	0.325	9.92	0.614	0.721	2.0	278	0.269
53	0.322	10.02	0.620	0.771	4.0	394	0.381
93.1 % acid at 194.4° C.							
54	0.319	8.25	0.523	10.65	10.0	158 ^d	0.144
55	0.318	7.79	0.494	10.50	20.0	259	0.236
56	0.322	8.10	0.514	1.20	3.0	281	0.256
57	0.319	7.19	0.456	1.22	5.0	365	0.334
58	0.320	9.56	0.606	0.716	2.0	259	0.251
85.2 % acid at 194.4° C.							
60	0.322	8.48	0.607	0.748	3.15	196 ^b	0.456
61	0.319	8.81	0.631	0.753	3.08	201	0.467
78	0.324	7.80	0.559	8.92	15.27	124	0.288
79	0.320	7.89	0.565	8.90	7.75	72	0.166
80	0.327	7.22	0.517	1.10	2.92	130	0.304
81	0.326	6.29	0.450	1.10	1.43	76	0.179

- a- spec. act. of acid, for this and succeeding runs, at zero time --1208 c./min.-mg. of BaSO₄
- b- spec. act. of acid, for this and succeeding runs, at zero time --446 c./min.-mg. of BaSO₄
- c- spec. act. of acid, for this and succeeding runs, at zero time --1066 c./min.-mg. of BaSO₄
- d- spec. act. of acid, for this and succeeding runs, at zero time --1141 c./min.-mg. of BaSO₄
- e- c./min.-mg. of BaSO₄

TABLE III
EXCHANGE RATES

Run #	Rate, m-moles per hr.	1/k', hrs.	R'
98.0 % acid at 194.4° C.			
6	0.0234	6.59	0.465
7	0.0233	5.99	0.416
8	0.0203	6.84	0.419
10	0.0199	7.08	0.424
11	0.0181	7.59	0.414
12	0.0141	6.27	0.267
13	0.0151	5.93	0.276
14	0.0124	6.97	0.263
15	0.0141	6.39	0.273
16	0.0129	6.11	0.238
19	0.0271	11.2	0.927
20	0.0284	10.8	0.929
21	0.0311	10.4	0.973
22	0.0232	3.55	0.0245
23	0.0189	4.17	0.0231
24	0.0189	4.19	0.0238
98.0 % acid at 167.5° C.			
66	0.000825	21.9	0.0567
67	0.000774	23.5	0.0572
68	0.00406	31.5	0.394
69	0.00377	32.0	0.377
70	0.00595	48.4	0.889
71	0.00552	48.8	0.830
98.0 % acid at 181.4° C.			
86	0.0154	17.4	0.836
94	0.00200	8.90	0.0552
95	0.00190	9.22	0.0552
96	0.00990	14.9	0.458
97	0.0137	20.0	0.855

Table III Continued

Run #	Rate, m-moles per hr.	1/k', hrs.	R'
98.0 % acid at 225.3° C.			
82	0.0216	0.852	0.0579
83	0.0222	0.811	0.0558
84	0.114	1.08	0.384
85	0.124	0.998	0.383
90.8 % acid at 225.3° C.			
88	0.0323	0.584	0.0594
89	0.0320	0.575	0.0580
90	0.211	0.700	0.465
91	0.200	0.732	0.460
90.8 % acid at 194.4° C.			
26	0.00450	3.42	0.0460
27	0.00444	3.50	0.0470
32	0.0542	5.03	0.842
33	0.0279	4.61	0.388
34	0.0332	3.86	0.386
35	0.0510	5.51	0.844
90.8 % acid at 167.5° C.			
72	0.000999	16.7	0.0522
73	0.000934	17.3	0.0510
75	0.00497	21.4	0.330
76	0.00867	31.0	0.837
77	0.00942	30.4	0.894
97.0 % acid at 194.4° C.			
36	0.00378	3.91	0.0459
37	0.00352	4.18	0.0461
38	0.222	5.79	0.402
39	0.0217	5.78	0.392
40	0.0345	8.44	0.908
41	0.0341	8.92	0.938

Table III Continued

Run #	Rate, m-moles per hr.	1/k', hrs.	R'
96.0 % acid at 194.4° C.			
42	0.00468	3.63	0.0519
43	0.00422	3.67	0.0477
45	0.0235	5.10	0.373
47	0.0372	7.35	0.854
94.9 % acid at 194.4° C.			
48	0.00442	3.47	0.0480
49	0.00467	3.44	0.0498
50	0.0281	4.54	0.396
51	0.0249	5.03	0.390
52	0.0493	5.63	0.852
53	0.0374	6.93	0.804
93.1 % acid at 194.4° C.			
54	0.00477	3.28	0.0491
55	0.00411	3.64	0.0470
56	0.0305	4.52	0.428
57	0.0248	4.81	0.374
58	0.0447	6.06	0.847
85.2 % acid at 194.4° C.			
60	0.0599	4.36	0.811
61	0.0628	4.25	0.838
78	0.00691	2.94	0.0627
79	0.00719	2.83	0.0635
80	0.0388	3.97	0.470
81	0.0424	3.15	0.410

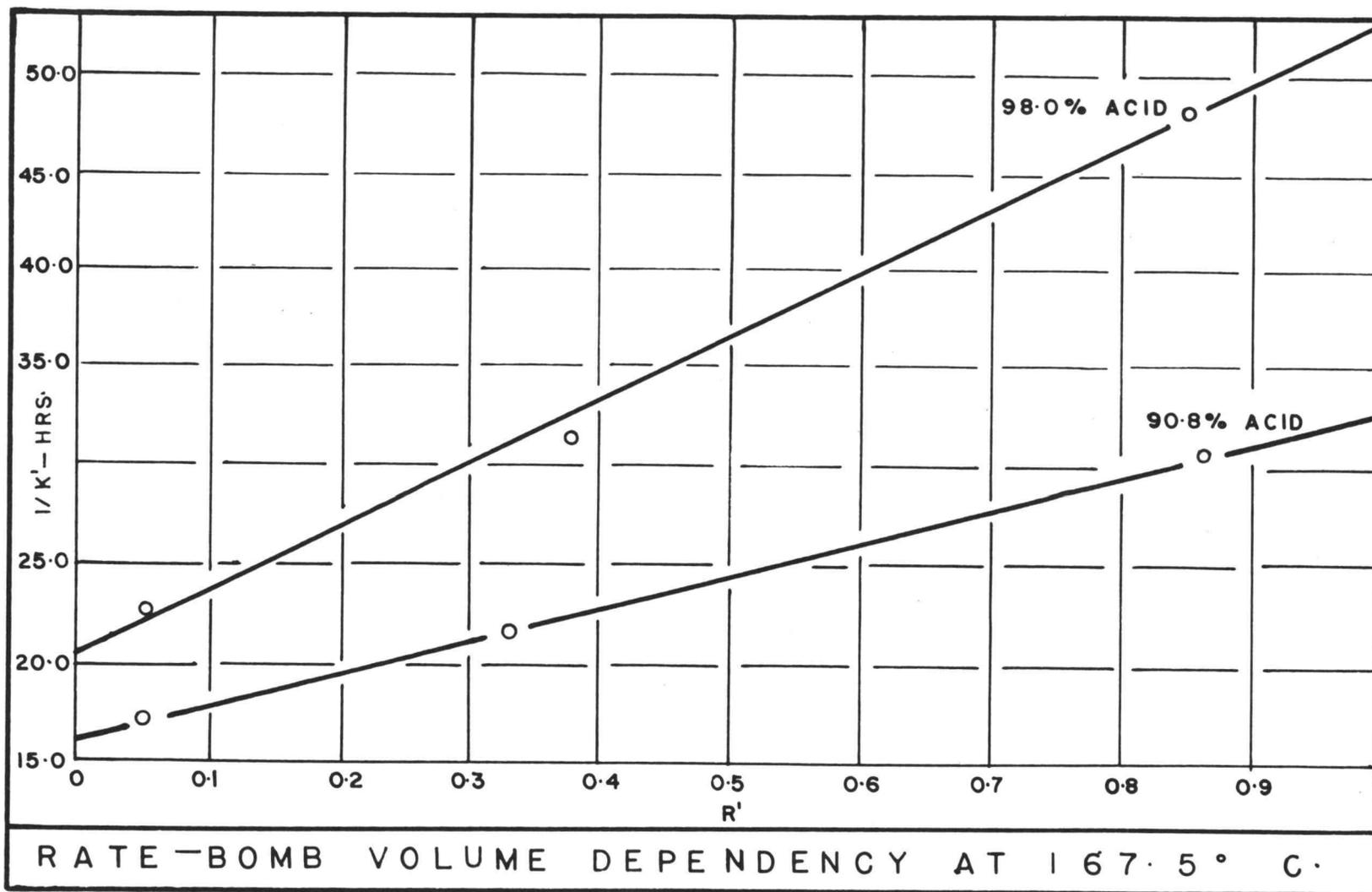


FIGURE 1

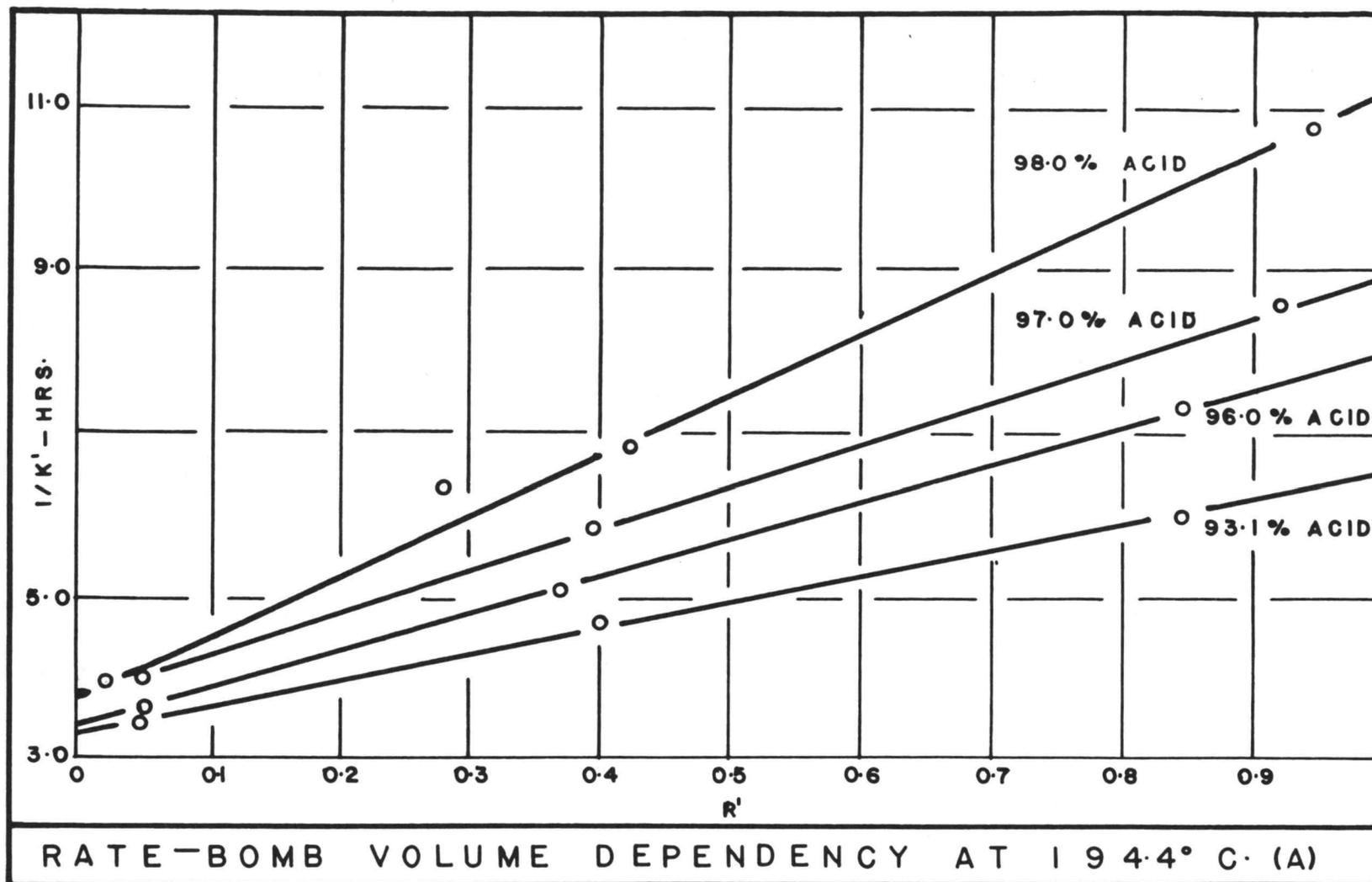


FIGURE 2

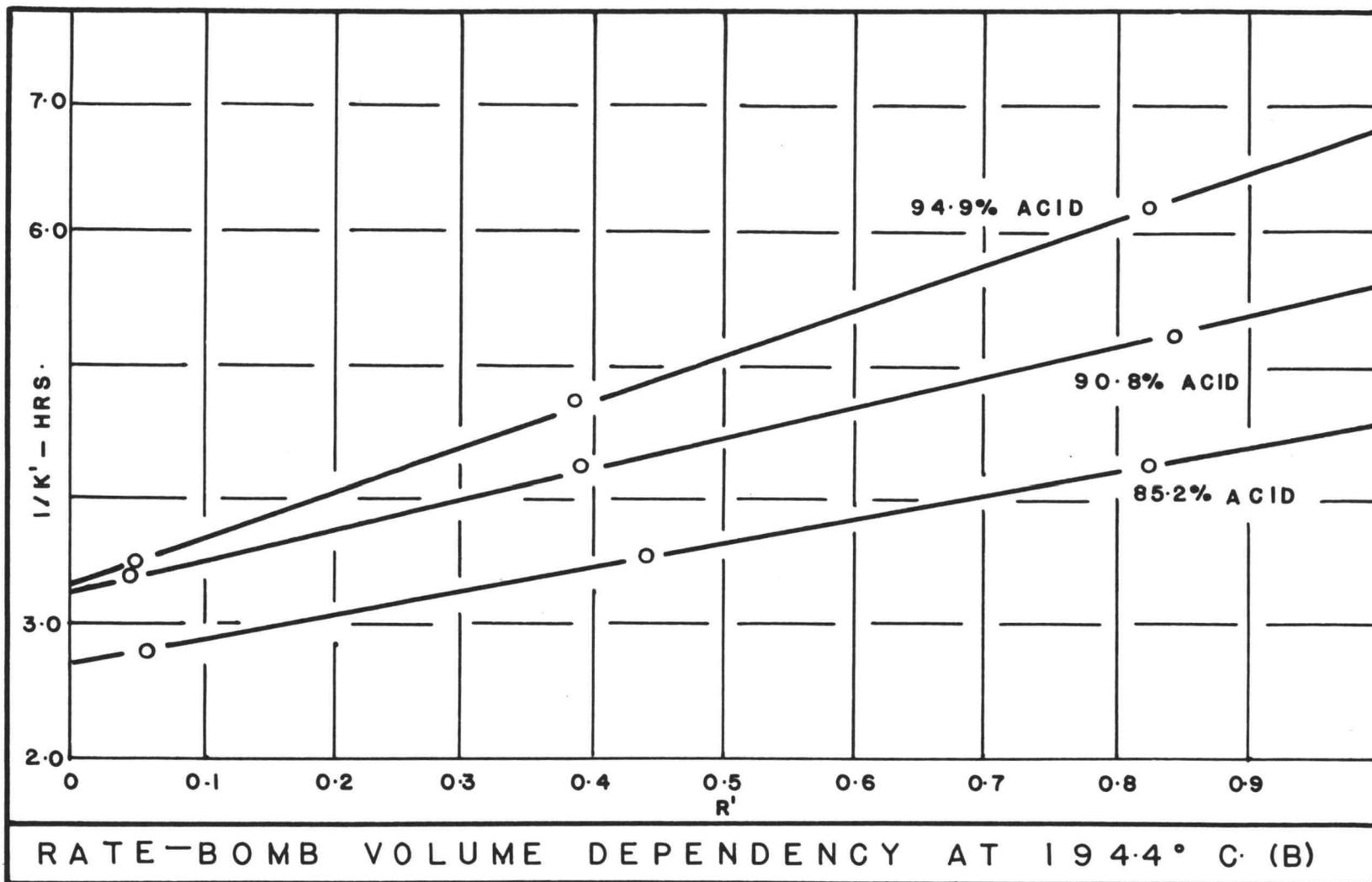


FIGURE 3

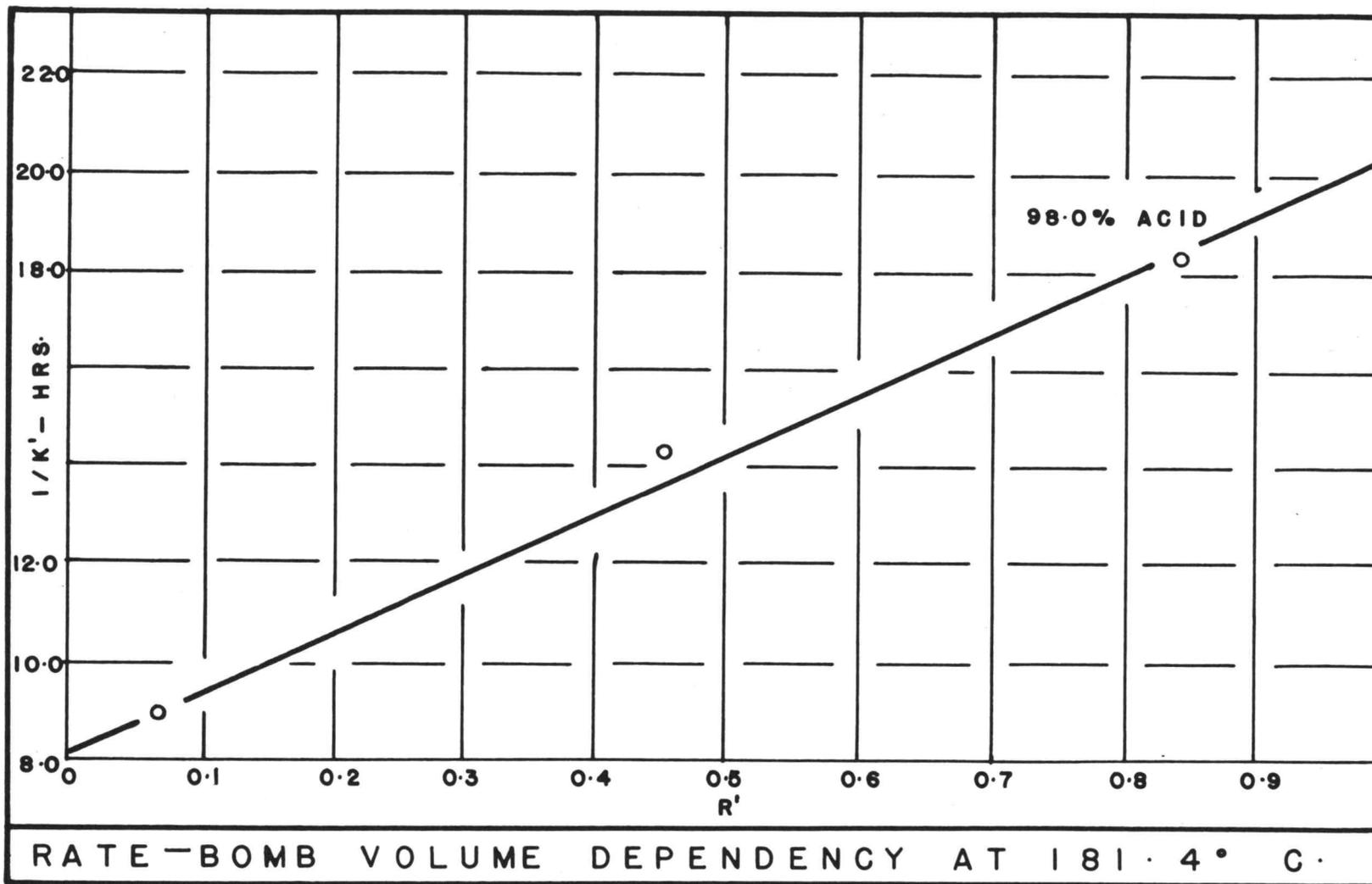


FIGURE 4

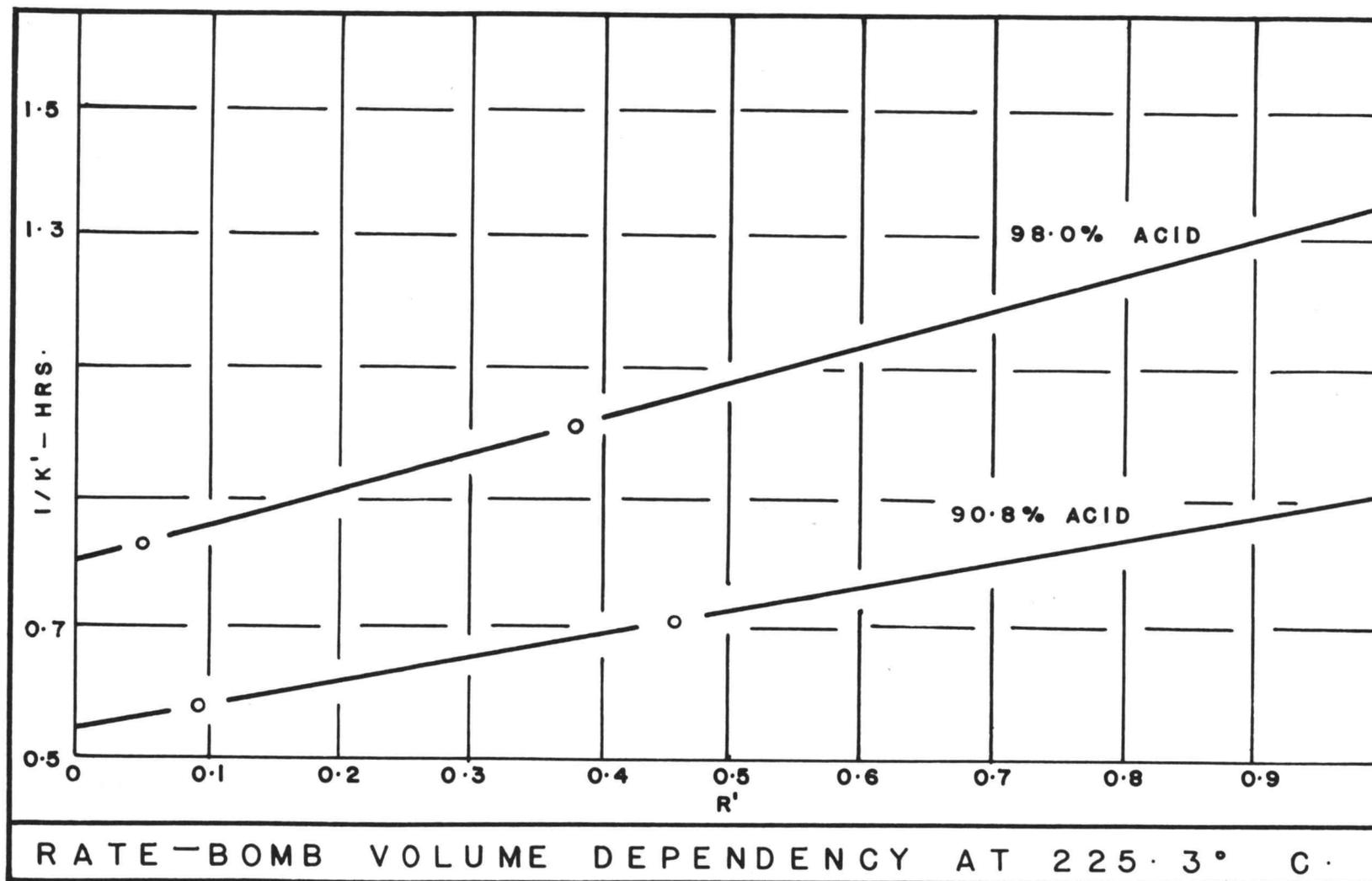


FIGURE 5

TABLE IV
SUMMARY OF c VALUES

Temp., ° C.	% acid	c
194.4	98.0	3.00
194.4	97.0	2.39
194.4	96.0	2.35
194.4	94.9	2.04
194.4	93.1	1.97
194.4	90.8	1.71
194.4	85.2	1.67
225.3	98.0	1.69
225.3	90.8	1.67
167.5	98.0	2.60
167.5	90.8	2.06
181.4	98.0	2.46

DISCUSSION

The possible effect on the solubilities, as determined, of non-ideality in the behavior of the sulfur dioxide as a gas and the non-ideality in the behavior of the solutions was considered, gas imperfections being of lesser importance, since deviations from ideality in the behavior of solutions is more probable. Calculations were carried out in order to determine the maximum pressure that could be encountered within any of the bombs, and this pressure turned out to be approximately thirteen atmospheres. Since the critical pressure of sulfur dioxide is 77.7 atmospheres and in view of the high temperatures involved in the work as opposed to a critical temperature of 157.2 degrees centigrade, it was felt that deviations of sulfur dioxide from ideal gas behavior in this case had no significant effect on the solubilities determined.

The possibility of a fugacity correction was nevertheless considered. Since practically all of the gas is dissolved in the smallest bombs and the pressure is quite low in the largest bombs, gas imperfections would be most significant for the intermediate size bombs. The fugacity of the sulfur dioxide was determined on this basis and calculations showed that for a given pressure the

concentration of the gas in the liquid might be up to approximately three percent lower than expected; however, since this is well within the experimental accuracy of the work, a fugacity correction was considered non-significant.

The applicability of Henry's Law to the present work was considered valid, due to the low molalities involved. The maximum molality encountered, if all the gas was dissolved, would be approximately 0.3 and this figure would be approached only in the case of the smallest of bombs. Deviations from Henry's Law would show up in the plots of $1/k'$ versus R' , in that straight lines would not be obtained (cf. Section II). Consideration of Figures 1 through 4 show that, within experimental accuracy, straight lines are the results of such plots. Furthermore, Masters (5)^c made a considerable number of exchange runs for 98.0 percent acid at 194.4 degrees centigrade with bomb volumes of from five to ten milliliters (and therefore low liquid to gas volume ratio). Here the molality is quite low and thus the validity of Henry's Law can be assumed. Extrapolation of the straight line drawn through a plot of $1/k'$ versus R' for the results of his work gave a value for c closely similar to that obtained in the present work, where a much wider bomb volume range was covered. In view of the foregoing two points, any deviation from ideal behavior of the solution was considered to be within the experimental

^c Same as the previous footnotes.

accuracy of this work, and so was disregarded.

Comparison of present results with those of earlier work mentioned in Section I showed some similarities and some contrasts. For comparison of solubility with acid concentration variation, it was found convenient to change from *c* values to grams of sulfur dioxide dissolved per hundred grams of sulfuric acid, this being the way the solubility data were reported in the earlier works. This was accomplished by direct translation of the definition of *c* by means of the ideal gas equation and density values appearing in Table I. A summary of these new values appear in Table V.

TABLE V
RELATIONSHIP OF SOLUBILITY UNITS

<u>% acid</u>	<u>c</u>	<u>% gas^a</u>
98.0	3.00	0.300
97.0	2.39	0.239
96.0	2.35	0.235
94.9	2.04	0.204
93.1	1.97	0.198
90.8	1.71	0.173
85.2	1.67	0.174

^a -grams of SO₂/100 grams H₂SO₄

A plot of the log of the solubilities versus acid concentration appears in Figure 6. Only enough values from the work of Miles and Carson (7, p.788) were read

from their graph to sketch in the curves for twenty and sixty degrees centigrade. These two curves are presented along with a plot of the results at 194.4 degrees centigrade from the present work, for comparison. The graph indicates a general conformity of trends observed in the current research with those of Miles and Carson: The solubility increases with increase of acid concentration and the rate of increase seems to become greater both with increase in concentration and with temperature; however, the rather sharp increase in the solubility in the region of ninety-eight percent acid for the present work is probably greater than would be expected from the earlier work. This point appears again later on in the discussion.

Another revealing basis of comparison of the present results with earlier work lies in considering the solubility variation with temperature at a particular acid concentration. To this end it was convenient to change solubility units of the earlier work from grams of sulfur dioxide dissolved per hundred grams of acid to c values. This was accomplished as explained before, using interpolated values for density and vapor pressure of sulfuric acid appearing in the International Critical Tables (10, pp.56-57, 302-304). These data are summarized in Table VI.

A plot of $\log c$ versus $1/T$ for 98.0 and 90.8 percent acid, showing points from the present work, from

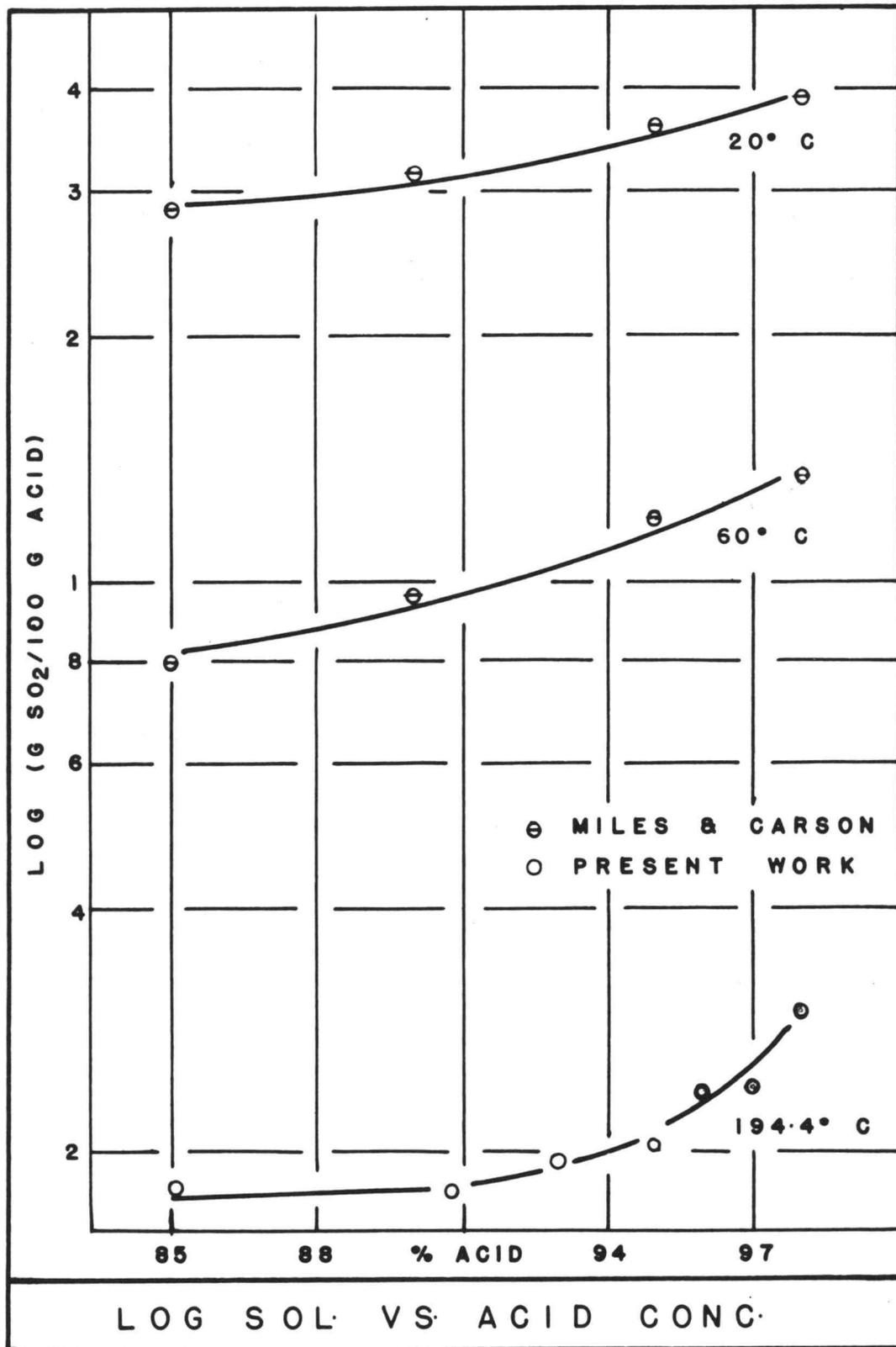


FIGURE 6

TABLE VI
CONVERSION OF EARLIER DATA TO c VALUES

Temp., ° C.	Gas sol., g/100 g	Acid v.p., mm Hg	Acid density	c	$1/T$
90.8% acid-Milbauer					
23	3.075	-----	1.814	21.1	0.00338
30	2.270	-----	1.808	15.9	0.00330
50	1.525	-----	1.787	11.3	0.00310
100	0.436	001.3	1.738	3.62	0.00268
150	0.171	015.4	1.689	1.60	0.00236
200	0.053	106.7	1.643	0.614	0.00211
237	0.040	378.8	1.608	0.838	0.00196
90.8% acid-Miles & Carson					
20	3.15	-----	1.818	21.5	0.00341
40	1.75	-----	1.798	12.6	0.00320
60	1.00	-----	1.777	7.58	0.00300
98.0% acid-Miles & Carson					
20	3.98	-----	1.836	27.4	0.00341
40	2.03	-----	1.816	14.8	0.00320
60	1.40	-----	1.798	10.7	0.00300

Milbauer (6, p.224), and from Miles and Carson (7, p.788) appear in Figure 7. Theory says that such a plot should produce a straight line, which Milbauer's data for 90.8 percent acid fit with some scattering at the higher temperatures, and Miles and Carson's points for 98.0 percent acid conform to for the short temperature range indicated; however, extrapolation to the lower temperature of the curves for the present work indicates a bending over of the graph or leveling off of the solubility at the higher temperatures for both acid concentrations.

It is evident that the results of the present investigation do not agree with those given by Milbauer for 90.8 percent acid, the only data in the literature which are available for comparison. Although it may be seen that Milbauer's two highest temperature points are of only low reliability, the source of the disagreement is not clear at this time.

The method used in the present instance was a static one and appears to be reliable. Milbauer's technique was a dynamic one, consisting of saturating the acid by a flow of gas and then chemically analyzing for dissolved gas. The very considerable vapor pressure of acid at the high temperatures may have introduced a complication in this procedure.

It seems evident that further investigation of this

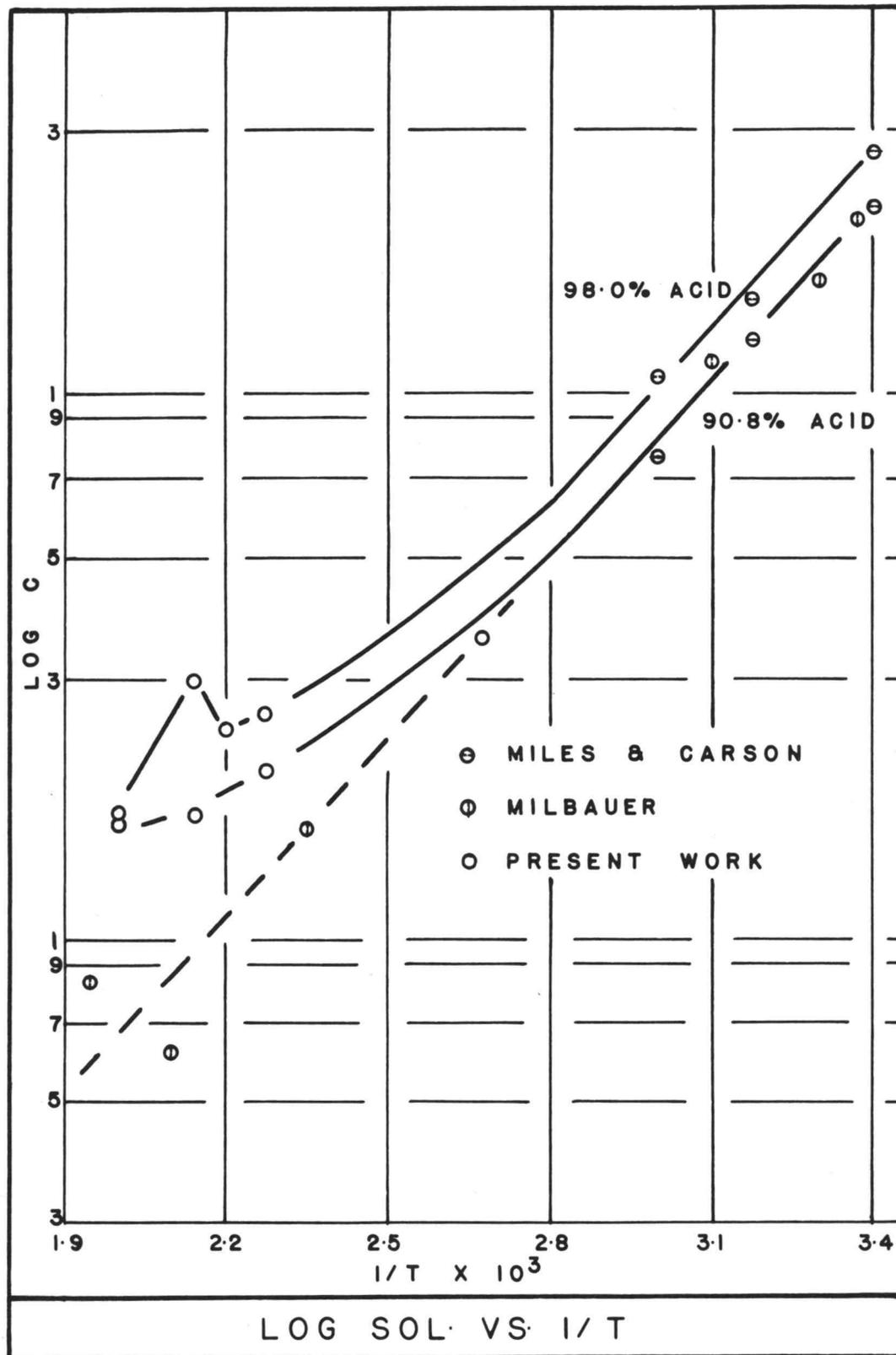


FIGURE 7

point will be necessary; specifically, solubility measurements by direct physical means seem in order. A start has already been made in this direction in this laboratory^d and there does appear to be some corroboration of a tendency of the solubility curve to level off in the manner of Figure 7, although the data so far available extend only to 170 degrees centigrade.

If the leveling off shown by Figure 7 is indeed real, it may possibly be more acceptable than one might at first assume. The idea that gas solubilities always decrease with temperature is based largely on experience with water solutions. It has been shown, by way of contrast, that in various organic solvents a number of gases of low solubility (inert gases, nitrogen, carbon monoxide, hydrogen and carbon dioxide) show a different behavior (3, pp.342-367 and 4, pp.68-80). Specifically where the Ostwald Coefficient (the same as c in this thesis) is less than unity, the solubility increases with temperature, and where it is greater than unity, it decreases with increase in temperature, but does not become less than one. Lannung (4, pp.68-80) suggests that there is here manifest a tendency for the Ostwald coefficient to approach the value one, i.e. a

^d Norris, T.H. Solubility measurements of sulfur dioxide in concentrated sulfuric acid. Chemistry department. Oregon State College. 1953. To be published.

uniform distribution of gas between gas and liquid phases, with higher temperatures.

On the basis of the foregoing, it seems possible that the behavior observed in the sulfur dioxide-sulfuric acid case may be another illustration of the same tendency since the leveling off shown by Figure 7 clearly occurs as the c value of unity is approached. Milbauer's data, it may be seen, suggest a steady decrease in c from large values to figures less than one. There seems evidently to be here an inviting area for further research.

On Figure 7 the point for 98.0 percent acid at 194.4 degrees centigrade seems either to be high or to suggest an additional irregularity in the plot. Since this particular point is based on many more observations than any of the other points, its position is probably correct, and one is left with the suggestion of an irregularity.

This in turn appears to suggest the setting in of some chemical change within the 98.0 percent acid in this temperature range. While there is no real evidence on the basis of which to speculate as to the nature of such a change, it is of some interest to note that it occurs in the general temperature region where the radiosulfur exchange reaction between the gas and the acid assumes an appreciable rate. It has been shown that sulfur dioxide at room temperature dissolves in concentrated sulfuric acid

without interaction (2, pp.2932-2934). Perhaps the rise at 194.4 degrees centigrade is indicative of the onset of a specific interaction of gas with acid.

The purpose of the research reported in this thesis has been two-fold as mentioned before. In addition to supplying certain high temperature solubility data not available in the literature, it has been useful in demonstrating the applicability of a novel technique for solubility determination. Further exploration of the possible usefulness of this technique would seem well worth while.

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