# Critical Temperatures and Densities of the $SO_3$–$H_2O$ System

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**The critical temperature and critical densities in the system $SO_3$–$H_2O$ are reported at concentrations from pure water to an $SO_3$ mole fraction of about 0.56. The critical temperature curve has a maximum of about 670° C. at an $SO_3$ mole fraction 0.38. Using van der Waals' concepts for binary liquid mixtures and assigning values to the van der Waals' constants for the pure components an empirical equation is derived which describes the data with a standard deviation of 3.6° C.**

VERY LIMITED experimental data concerning the critical region of two-component aqueous systems are available. The technical difficulties of reaching states of true phase equilibrium, of the accurate control and measurement of relatively high temperatures and pressures, and especially of problems relating to the highly corrosive nature of most aqueous systems are evident. The system $SO_3$–$H_2O$ was selected for study because of this laboratory's interest in sulfate solutions at elevated temperatures, because it represented a common material for which no critical data were available, because of the known strong interaction between the components, and because preliminary experiments indicated that materials were available which would adequately resist corrosion.

The critical point for a one-component system may be defined as the limiting conditions under which the two phases have identical properties (*7*). This is the highest temperature and pressure at which the two phases may coexist. However, for a two-component system critical phenomena occur over a limited range of temperatures and pressures, and do not correspond necessarily to either the highest temperature or the highest pressure at which the phases may coexist (*4, 10*).

The additional degree of freedom, obtained as a consequence of the presence of a second component, may be expressed by the mole fraction along with the volume fraction of the liquid phase (at 25° C.) in a constant volume apparatus (*10, 11*). The liquid volume fraction is referred to hereinafter as fraction filling. The original intent in this work was to observe, in one set of experiments, the temperature and position of the vanishing meniscus as functions of mole fraction and fraction filling (25° C.). In a second series of experiments, vapor pressure was to be observed as a function of the same parameters and temperature. By virtue of the common parameters, corresponding critical temperatures, pressures, and volumes could be selected. This first portion of the work has been completed and the critical temperatures reported here are the observed or interpolated values at which the line of demarcation between the liquid and vapor phases becomes indistinguishable at the mid-point of the sample tube when viewed through a telemicroscope.

## EXPERIMENTAL

The apparatus for critical temperature measurements was a modification of that described by Marshall *et al.* (*6*) for semimicro phase studies above atmospheric pressure. Modifications included use of a graphite cylindrical furnace for temperatures near the melting point of aluminum and use of fused silica tubing for constant volume containers to eliminate the rapid corrosion of borosilicate glass by hot acid solutions.

Since the fraction filling at room temperature for a single tube could not be accurately controlled, numerous sample tubes with random fraction fillings were reported. A sample tube of known fraction filling and containing the solution of known concentration was placed in the furnace at a temperature a few degrees below the approximate critical temperature as determined by the behavior of previous sample tubes used in preliminary work. The temperature was increased steadily until the meniscus disappeared and was then decreased until the meniscus reappeared. The observed rising and falling temperatures differed by less than 0.1° C.

The fraction filling at room temperature *vs.* fraction filling at the disappearance of the meniscus was plotted, Figure 1. The proper room temperature fraction filling which should result in the disappearance of the meniscus at the center of the sample tube was obtained from the graph. This value was used on the temperature *vs.* room temperature fraction filling graph to give the value of the critical temperature as defined.

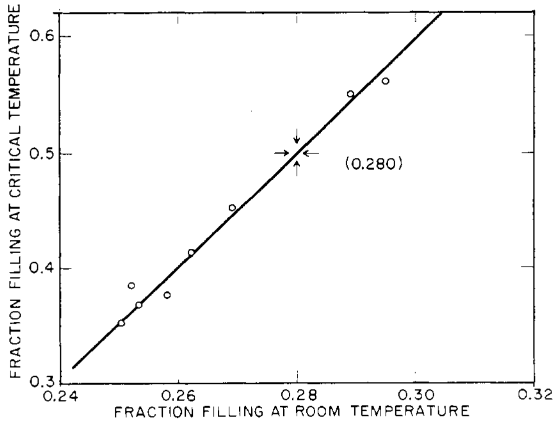

Figure 1. Relation between fraction filling at room temperature and at disappearance of meniscus, $X_{SO_3} = 0.4353$

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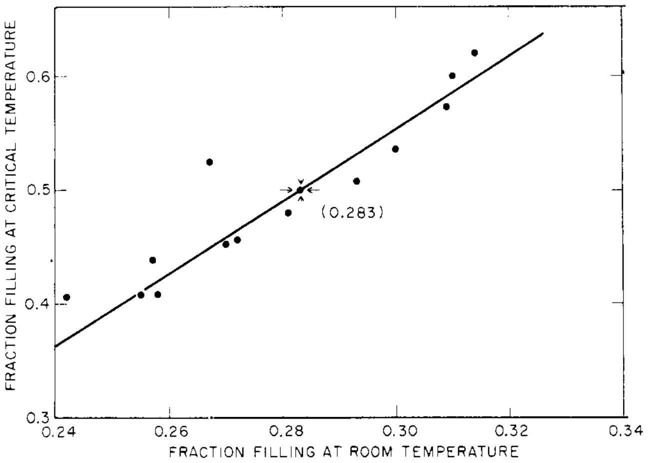

Figure 2. Relation between fraction filling at room temperature and at disappearance of meniscus, $X_{SO_3} = 0.3368$

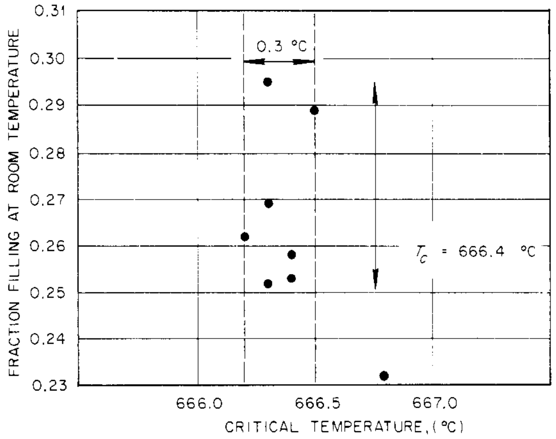

Figure 4. Temperatue at which meniscus disappeared as function of fraction filling, $X_{SO_3} = 0.4353$

## RESULTS

Figure 2 illustrates the relationship between the fraction filling at room temperature and the fraction filling when the meniscus disappeared. The correct room temperature filling resulting in the meniscus disappearing in the center of the sample tube can be inferred from the graph. The relationship between the temperature at which the meniscus disappeared and the fraction filling is shown in Figure 3 for the same solution. The critical temperature is based on the fraction filling read from the previous graph.

As the solution under study approaches 50 mole %, the dependence of critical temperature on fraction filling decreases, and the critical temperature becomes practically independent of the fraction filling. This is illustrated by Figure 4, and the trend is illustrated by comparison of Figure 4 with Figure 3.

Work with solutions above 50 mole% was difficult. No satisfactory method was devised for producing such solutions and transferring them to the sample tubes or for preparing the solution directly inside the tubes. Therefore, only one measurements was successful and that was on fuming $H_2SO_4$ solution. Here again the temperature at which the meniscus disappeared was dependent on the fraction filling.

Table I and Figure 5 summarize the data obtained. The fraction filling at room temperature which resulted in the

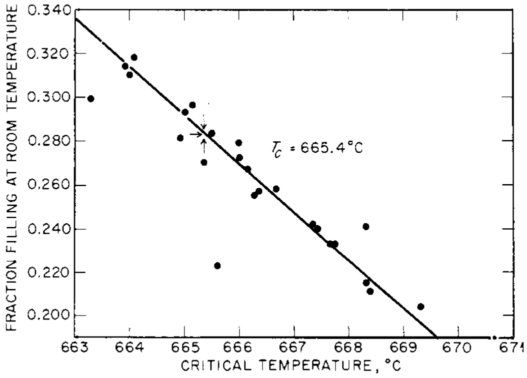

Figure 3. Temperature at which meniscus disappeared as function of fraction filling, $X_{SO_3} = 0.3368$

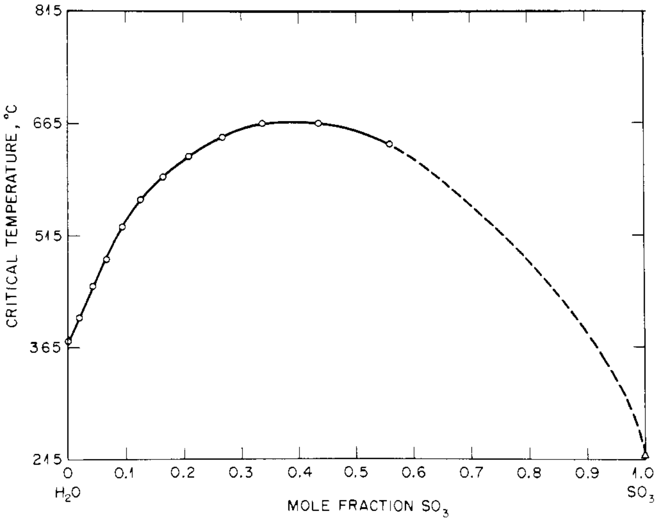

Figure 5. Critical temperature dependence on concentration

Table I. Critical Densities and Critical Temperatures for the $SO_3$–$H_2O$ System

| Mole Fraction $SO_3$ | Density, (25° C.) Grams/Cc. | Liquid Fraction,[a] (25° C.) | Critical Density, Grams/Cc. | Critical Temperature, ° C. Obsd. | Calcd. |
|---|---|---|---|---|---|
| 0.0000 | 0.997 | 0.321 | 0.320 | 374.2[b] | 374.2 |
| 0.0193 | 1.065 | 0.393 | 0.419 | 404.2 | 410.6 |
| 0.0419 | 1.139 | 0.396 | 0.451 | 447.4 | 449.0 |
| 0.0654 | 1.211 | 0.376 | 0.455 | 482.8 | 484.3 |
| 0.0938 | 1.291 | 0.353 | 0.456 | 526.1 | 521.6 |
| 0.1251 | 1.372 | 0.336 | 0.461 | 562.0 | 556.5 |
| 0.1643 | 1.467 | 0.333 | 0.489 | 592.2 | 592.3 |
| 0.2084 | 1.565 | 0.314 | 0.491 | 621.0 | 623.3 |
| 0.2664 | 1.676 | 0.293 | 0.491 | 646.8 | 651.4 |
| 0.3368 | 1.778 | 0.283 | 0.503 | 665.4 | 669.0 |
| 0.4353 | 1.833 | 0.280 | 0.513 | 666.4 | 668.3 |
| 0.5591 | 1.784 | 0.331 | 0.591 | 637.2 | 632.0 |
| 1.0000 | 1.884 | 0.336 | 0.633 | 218.3[c] | 218.3 |

[a] The fraction filling at 25° C. which yields a liquid fraction of 0.5 at the critical temperature. [b] From Ref. 3. [c] From Ref. 1.

meniscus disappearing at the center of the tubes and the corresponding critical temperatures are recorded.

The critical temperature curve is approximately parabolic and suggests that the data could be empirically expressed by a quadratic function of the mole fractions. Evaluation of the three constants of a simple quadratic by least squares yields an equation which describes the data very poorly (Standard error of estimate is about 16°). A much more satisfactory equation was derived by consideration of van der Waals' treatment of binary liquid mixtures (*8, 10*). In essence, the procedure outlined below permits use of a six constant equation in which four of the constants can be assigned values obtained from the available *P-V-T* data for the pure components. The remaining two constants can then be determined by the least squares method from our data for the binary system.

van der Waals' equation of state for binary mixtures gives:

$$T_c = \frac{8a_x}{27R\,b_x} = k\,\frac{a_x}{b_x} \tag{1}$$

where

$$a_x = a_1X_1^2 + 2a_{12}X_1X_2 + a_2X_2^2 \tag{2}$$

$$b_x = b_1X_1^2 + 2b_{12}X_1X_2 + b_2X_2^2 \tag{3}$$

$X_1$ and $X_2$ are the mole fractions of water and $SO_3$, respectively. From the critical constants for water (*3*) and $SO_3$ (*1*) the following values are assigned.:

$a_1 = 5.4657$ $\quad a_2 = 8.2045$

$b_1 = 0.03049$ $\quad b_2 = 0.06029$

Substitution of these values into Equations 1, 2, and 3 followed by a least squares calculation of $a_{12}$ and $b_{12}$ from the data yields an equation which describes the data less accurately than the simple quadratic.

The van der Waals' constants, *a* and *b*, are not truly constants for most substances and especially for an associated liquid such as water. They are functions of both temperature and pressure. The *P-V-T* data for water published by Kennedy (*12*) permit an estimation of $a_1$ and $b_1$ in the range of interest. The most significant dependency shown is that of $a_1$ as a function of temperature and this can be approximated by assuming linear dependency. Analogous data for $SO_3$ are not available. As a compromise between mathematical simplicity and the desire to describe the data more accurately, we have assumed that all *b* values are constant and that all *a* values are linear functions of temperature with a slope indicated by the data for water. We obtained the following values:

For $H_2O$: $a_1$ (at $T_c = 647.3°$ K.) $= 5.4657$

$$a_1 = a_1' - a_tT = 7.574 - 0.00325T \tag{4}$$

$b_1 = 0.03049$

For $SO_3$: $a_2$ (at $T_c = 491.4°$ K.) $= 8.2045$

$$a_2 = a_2' - a_tT = 9.805 - 0.00325T \tag{5}$$

$b_2 = 0.06029$

For the mixture:

$$a_{12} = a_{12}' - a_tT = a_{12}' - 0.00325T \tag{6}$$

Substitutions from Equations 2, 3, 4, 5, and 6 into Equation 1 and rearrangement yields:

$$[T_c(a_tk + b_1) - a_1'k]\,\frac{X_1}{X_2} + [T_c(a_tk + b_2) - a_2'k]\,\frac{X_2}{X_1} = 2k\,a_{12}' - (2b_{12} + 2a_tk)\,T_c \tag{7}$$

All of the terms in the left side of Equation 7 have been assigned numerical values, and the entire function can be reduced to a numerical value for each set of experimental values for the mole fraction and the critical temperature. Application of the least squares method to Equation 7 yields values of $a_{12}' = 24.6305$ and $b_{12} = 0.06087$. The very large value for $a_{12}'$ is no doubt a reflection of the very strong chemical interaction between $SO_3$ and $H_2O$ and, therefore, indicates the system is very poorly represented as an ideal van der Waals' system.

Substitution of all the numerical values for the constants into Equation 7, elimination of $X_1$, and rearrangement yields the final empirical equation:

$$T_c\,(°\,\text{K.}) = \frac{27.3474 + 123.1719X_2 - 115.1164X_2^2}{0.04225 + 0.06076X_2 - 0.03096X_2^2} \tag{8}$$

The values for $T_c$ tabulated in the last column of Table I were calculated by Equation 8. The standard error of estimate is 3.6° C.

The acid system had some corrosive effects on the fused silica tubing at elevated temperatures. Figure 6 shows the time-critical temperature elevation relationship for several dilute solutions. More concentrated solutions had less effect on the glass even though the critical temperatures were higher. Because measurements could be made in approximately two minutes, no corrections were applied for corrosive effects.

Room temperature densities of each solution and the fraction filling permitted calculation of the critical densities. Table I and Figure 7 summarize the densities of the single phase remaining when the meniscus disappeared at the center of the tube.

A review of all graphs of temperature *vs.* fraction filling at room temperature shows a marked difference in the slopes of the curves for different concentrations. At low $SO_3$ concentration, the liquid composition would change rapidly if the vapor phase were chiefly water. At high $SO_3$ concentrations, the liquid composition would change rapidly if the vapor were chiefly $SO_3$; at concentrations near 50

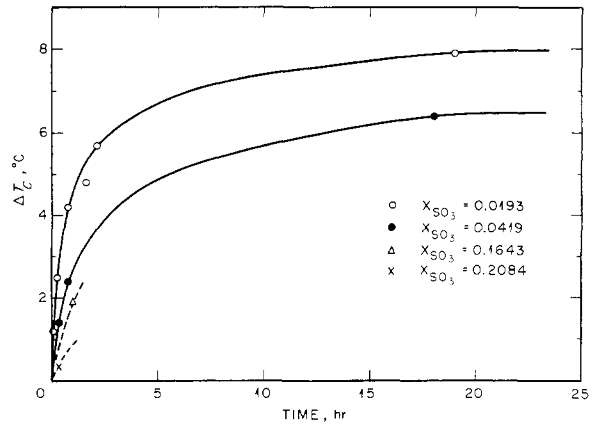

Figure 6. The effect of corrosion on the critical temperature

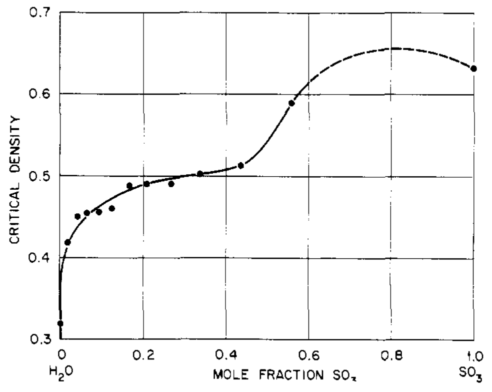

Figure 7. Critical density dependence on concentration

mole %, the liquid composition would not change materially if both components vaporized in approximately a 1:1 ratio. These suppositions are supported by this work, by vapor-liquid equilibrium data at lower temperatures (*9*) and by the work of Luchinskii (*5*).

The maximum in the critical temperature *vs.* composition curve is near 40 mole % $SO_3$. This is a shift in the water rich direction from the position of the maximum boiling point at one atmosphere. Luchinskii indicates a slight shift in the same direction of the single azeotropic point in a temperature range up to 200° C.

## LITERATURE CITED

(1) Berthoud, A., *J. Chim. Phys.* **20**, 77 (1923).
(2) Kennedy, G.C., *Am. J. Sci.* **248**, 540 (1950).
(3) Kobe, K.A., Lynn, Emerson, Jr., *Chem. Reviews* **52**, 117 (1953).
(4) Kuenen, J.P., *Z. physic Chem.* **24**, 667 (1897).
(5) Luchinskii, C.P., *Zhur. Fix. Khim.* **30**, 1207 (1956).
(6) Marshall, W.L., Wright, Henry W., Secoy, C.H., *J. Chem. Educ.* **31**, 34 (1954).
(7) Ramsay, W., *Proc. Roy. Soc. London* **30**, 323 (1880).
(8) Rutgers, A.J., "Physical Chemistry," 1st Eng. ed., p. 457, Interscience, New York, 1954.
(9) Thomas, J.S., Baker, W.F., *J. Chem. Soc. London* **127**, 2820 (1925).
(10) van der Waals, J.D., Kohnstamm, F., "Lehrbuck der Thermostatik," p. 140, Verlay Barth, Leipzig, 1927.
(11) White, David, Friedman, A.S., Johnston, H.L., *J. Am. Chem. Soc.* **72**, 3565 (1950).

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