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SOLUBILITY OF SULFUR DIOXIDE IN SULFURIC ACID

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OF POOR QUALITYKarl K. Chang, Leslie E. Compton and Daniel D. Lawson
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The solubility of sulfur dioxide in 50% (wt./wt.) sulfuric acid was evaluated by regular solution theory, and the results verified by experimental measurements in the temperature range of 25°C to 70°C at pressures of 60 to 200 PSIA. The percent (wt./wt.) of sulfur dioxide in 50% (wt./wt.) sulfuric acid is given by the equation $\%SO_2 = 2.2350 + 0.0903P - 0.00026P^2$ with P in PSIA.

INTRODUCTION

There are five thermochemical water splitting cycles that have been extensively investigated (see notes). They all have in common sulfur dioxide and sulfuric acid as part of the cycle in concentration ranges of 50 to 60%. Laboratory bench scale units have been assembled and in all cases operated at ambient pressures. In any large scale-up to practical commercial units the process pressures must be increased so that:

1. Gains in process efficiencies can be achieved.
2. The hydrogen and oxygen can be produced at high pressures to avoid the costs of pumping.

On review of the literature very little data exists on the solubility of sulfur dioxide in sulfuric acid (1,2,3). All of these data are at low pressures of sulfur dioxide in sulfuric acid, and the data given by Simeck et. al. was shown to follow Henry's Law (3). Because of the importance of this information we have calculated the solubility of sulfur dioxide in 50% (wt./wt.) sulfuric acid. To verify these calculations, measurements of the solubility of the gas in the acid were undertaken in the temperature range of 25°C to 70°C at pressures of 60 to 200 PSIA.

MISCIBILITY OF LIQUID SYSTEMS

In general, solubility, or miscibility of two liquids, is to be expected if there is a decrease in the free energy of mixing, i.e..

$$\Delta F_{mix} = \Delta H_{mix} - T\Delta S_{mix} \quad (1)$$

Inasmuch as the entropy of mixing ΔS_{mix} is always positive (i.e., $-T\Delta S_{mix} < 0$), the enthalpy of mixing ΔH_{mix} will virtually determine solubility. The latter term for non-polar and some polar substances is positive and its magnitude is proportional to the difference of the respective solubility parameters, δ , which are the square roots of the cohesive-energy densities.

$$\Delta H_{mix} = (\delta_1 - \delta_2)^2 \quad (2)$$

Thus, the closer the solubility parameters values, the smaller ΔH_{mix} will be and, consequently, the greater the decrease in ΔF_{mix} .

For the condition of liquid immiscibility the following approximation was obtained by Hildebrand and Scott (4).

$$\Delta H_{mix} = V (\delta_1 - \delta_2)^2 > 2RT \quad (3)$$

If an approximation is made for V by using the arithmetic mean of V_1 and V_2 when $V_1 \neq V_2$, then the expression becomes:

$$\frac{1}{2} (V_1 + V_2) (\delta_1 - \delta_2)^2 > 2RT \quad (4)$$

$$Q = \frac{1/2 (V_1 + V_2) (\delta_1 - \delta_2)^2}{2RT} \quad (5)$$

If the quotient Q is greater than 1, then the inequality of Equation 4 is satisfied and the liquids are immiscible.

These equations or approximations are to be regarded as a first order estimation or guide in the determination of miscibility of a system and should be experimentally verified if practical.

An estimation of the miscibility of sulfur dioxide (50% (wt./wt.)-sulfuric acid as per Equation (5) at 25°C (298K) is obtained from the results of the calculations shown in Equation 6):

$$Q = \frac{1/2 (46.79 + 35.67) (20.80 - 10.75)^2}{2 \times 1.986 \times 298} = 3.25 \quad (6)$$

Evaluation of terms in Equation 6 is shown in Table 1. The calculated value of Q in Equation 6 exceeds 1. Therefore sulfur dioxide is not completely miscible in 50% (wt./wt.) sulfuric acid. Figure 1 is a photograph of a two-phase-liquid system using the 50% H_2SO_4 . For concentrated sulfuric acid the calculated value of Q is 2.31. This result suggests that sulfur dioxide is more soluble in concentrated sulfuric acid.

Table 1. Values of Solubility Parameters and Molar Volumes

Material	Solubility Parameter, δ	Molar Volume, V cc/g-mole	Remarks
H_2SO_4 (25°C)	18.14	53.28	δ calc'd from vapor pressure data (5)
SO_2 (25°C)	10.75	46.79	δ calc'd from Antoine equation constants (5)
H_2O	23.46	18.069	δ calc'd as above (5)
$H_2SO_4-H_2O$ 50% (wt./wt.)	20.80	35.67	δ calc'd by the method of Gjaldbaek (6)

EXPERIMENTAL

The volume of the glass ampule used in this experiment was first calibrated with known amounts of water. Then a known quantity of 50% sulfuric acid was placed in the ampule along with a magnetic stirring bar. Sulfur dioxide was subsequently condensed into the ampule at liquid nitrogen temperature, and the ampule was sealed. The system was slowly heated and allowed to come to equilibrium at each measurement temperature. Care was exercised to avoid the formation of emulsions. The experimental apparatus is shown in Figure 2.

A quadratic regression analysis performed on the data gave the following equation

$$\% SO_2 = 2.2350 + 0.0903P - 0.00026P^2 \quad (7)$$

where P is the vapor pressure of sulfur dioxide from 60 to 200 psia (Figure 3).

CONCLUSION

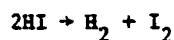
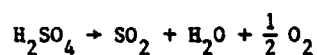
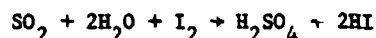
The results show that the solubility of sulfur dioxide in sulfuric acid deviates from Henry's Law at higher pressures (Figure 3) (3).

ACKNOWLEDGMENT

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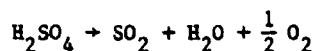
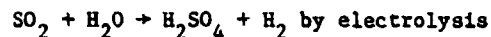
NOTES

1. The General Atomics Sulfur-Iodine cycle is described by:



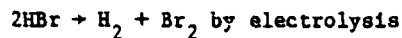
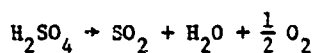
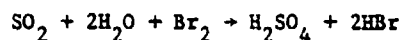
2. Ispra Mark 16 cycle is conceptually the same as the General Atomic cycle.

3. The Westinghouse Hybrid Sulfuric acid cycle is represented by:



4. The Ispra Mark 11 cycle is conceptually the same as the Westinghouse Hybrid cycle.

5. A representation of the Ispra Mark 13 Sulfur-Bromide Hybrid cycle is given by the following:

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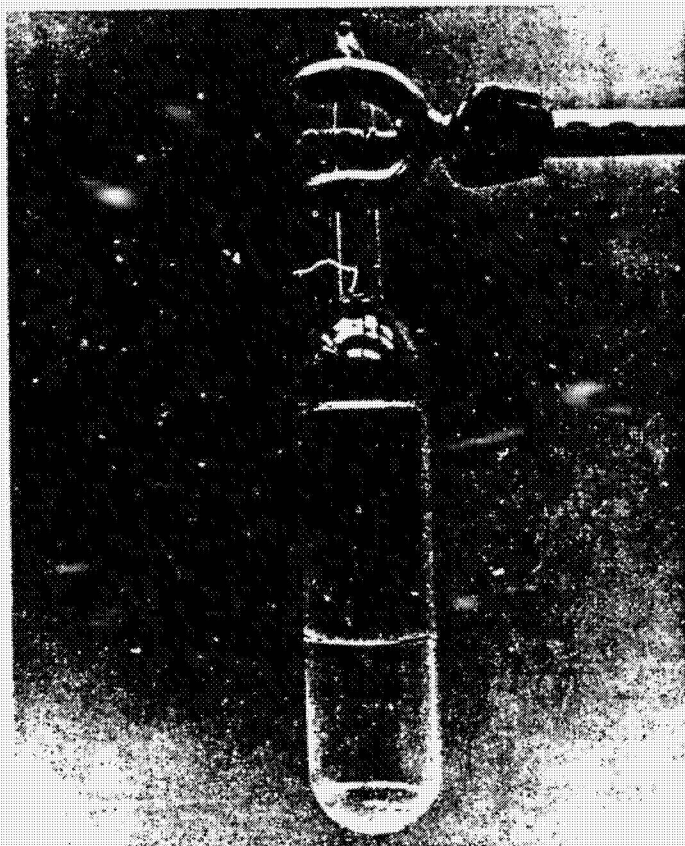


Figure 1. Sulfuric acid (50% wt./wt.) and liquid sulfur dioxide. The top phase is sulfur dioxide and bottom phase is the acid.

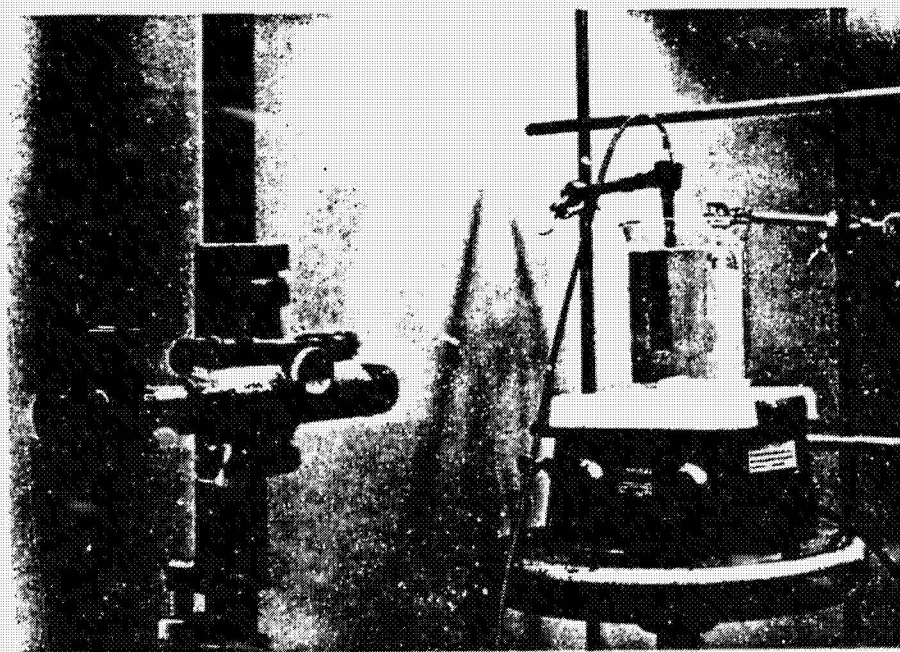


Figure 2. Experimental apparatus for measuring solubility of sulfur dioxide in sulfuric acid. The Gaertner cathetometer is accurate to ± 0.005 cm. Temperatures were measured to $\pm 0.01^\circ\text{C}$ with a Dymec quartz thermometer.

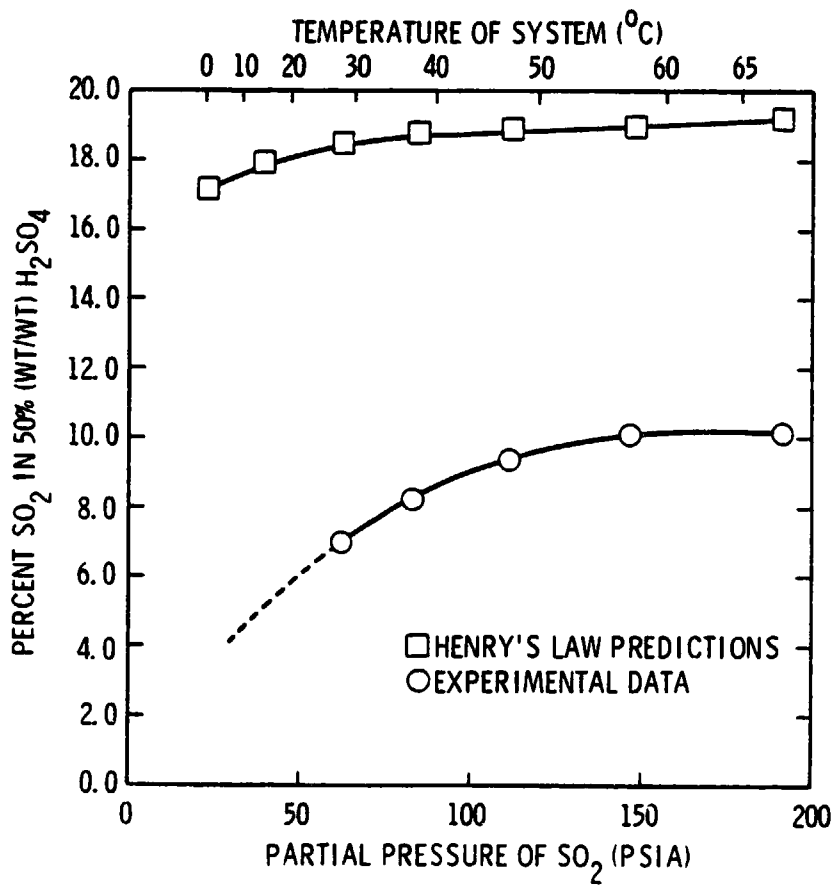


Figure 3. The solubility of sulfur dioxide in (50% wt./wt.) in sulfuric acid.