

# Automated constant pressure reactor for measuring solubilities of gases in aqueous solutions

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An automated constant pressure reactor for measuring the solubilities of slightly soluble gases in aqueous solution is described. The apparatus can also be used for kinetic studies of aqueous reactions involving a gaseous reactant or product. The system can be operated unattended and therefore can be used for prolonged experimentation. Results obtained using the apparatus for solubilities of methane and butane in triple distilled water at atmospheric pressure and 25°C are compared with those reported in the literature.

## INTRODUCTION

The solubilities of gases in aqueous solutions have been determined in the past using various methods.<sup>1-6</sup> One of the simple and reasonably accurate methods involved saturating a sample of solution with a given volume of gas and then measuring the volume of the undissolved gas. On the basis of this method Ben Naim and Baer<sup>6</sup> developed a technique in which the solubility of the gas was measured as the volume changes at manually maintained constant pressures. The technique was however unsuitable for long-term studies because of the continuous attention that was needed. The variation in pressure in between each manual adjustment was also an undesirable feature. An automated set up with several additional features suitable for interfacial chemistry work was therefore developed and tested in this study. The apparatus was used for measuring solubilities of methane and butane in water and surfactant solutions.

## APPARATUS

The apparatus developed is based on that of Ben Naim and Baer.<sup>6</sup> It consists essentially of an absorption cell, a gas volume measuring column and the pressure control system. The major features of the present system include the automation of the set up for maintaining a constant gaseous pressure and modifications for making the operation flexible and the apparatus adaptable for exchange of various parts. A schematic diagram of the apparatus is given in Fig. 1 and the major parts are described below.

### Absorption cell

The absorption cell consists of a 400 cc container connected at the side to two graduated tubes C1 and C2 and at the top center to another graduated tube C3, and all the graduated tubes are connected to each other and to the gas inlet. This cell, shown in Fig. 2, is similar to that used by Hung,<sup>7</sup> except for the fact that the Teflon needle valve No. 1 is connected eccentrically to bulb A1. This arrangement prevents accidental rapid flow of liquid during degassing into pressure sensing compartment E and the gas volume measurement column F shown in Fig. 1. Another Teflon needle valve No. 2 is connected to bulb A2 for filling the solution into the cell. The container is also provided with a Teflon O-ring joint D near the bottom to facilitate the introduction of the Teflon-coated stirring bar SB as

well as any solid particles or powder that is to be immersed in the liquid during the dissolution. Transfer of solid samples into the container and out of it is necessary, for example, for studying the effect of dissolved hydrocarbons on the floatability of mineral particles.<sup>8</sup>

Mixing of the solvent with the gas is achieved by pumping of the solvent through the side arm of the container to the top of the center arm owing to the centrifugal forces produced by the stirrer and then back into the container owing to the vortex generated during the stirring. The circulation of the solvent in this manner continuously produces large amount of fresh liquid-gas interfacial area allowing rapid approach to equilibrium. The design has also the advantage that before the actual commencement of the experiment, very little gas is absorbed since when the solution is not stirred the gas is in contact with the solvent only at three points in the small capillaries in the side arms and the center arm.

The volume calibration of the absorption cell up to the top of the capillary tubes of C<sub>1</sub>, C<sub>2</sub>, and C<sub>3</sub> is done by

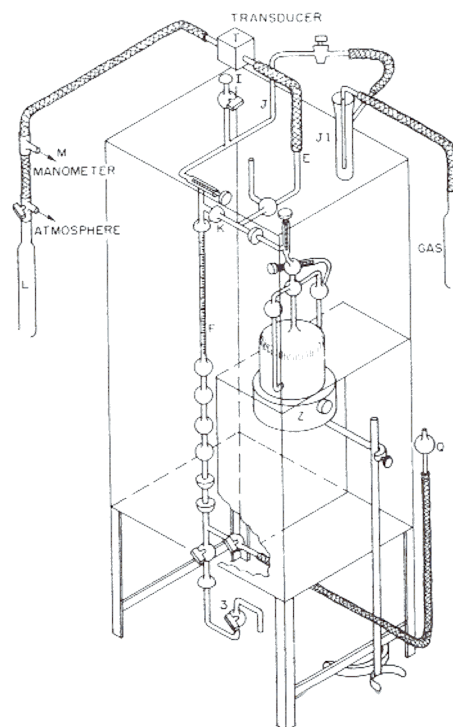


FIG. 1. General arrangement of the solubility apparatus.

weighing water into it at various levels at the given temperature.

### Gas Volume Measuring Column

The gas volume measuring column F shown in Fig. 1, is constructed in three parts. The lower portion of the column is connected to the mercury reservoir Q. Stopcock No. 3 ensures easy withdrawal of mercury from the system for various purposes including calibration of the bulbs. The top portion consists of points to the absorption cell K, vacuum system I and the gas inlet J.

The main mercury column consists of four glass bulbs of approximately 6.5 ml capacity each, sealed to a microburette, of about 10 ml capacity graduated to 0.05 ml. A major advantage of the present gas volume measuring column is that the central mercury column can be replaced with columns of different capacities depending on the solubility of the gas concerned. It might be mentioned that for increased accuracy initial and final mercury levels in the column were read using a cathetometer.

### Pressure Control System

The necessity of maintaining a constant pressure of the dissolving gas arises from the fact that solubility of the gas depends on its partial pressure in the system. In the previous studies,<sup>6-8</sup> to achieve this, the mercury level in the gas volume measuring column had to be manipulated manually to maintain constant pressure. This of course is a time consuming intermittent operation and, because of the personal attention required, is of limited use for prolonged kinetic studies. Furthermore, in the previous studies, effect of variations in the atmospheric pressure on the experimental observations appears to have been ignored.

The pressure control system shown in Fig. 3 consists of a "Pace" transducer T ( $\pm 0.1 \text{ kg cm}^{-2}$ ), transducer demodulator-indicator R, an electrical relay N, and a motor speed controller O which is energized by the relay and controls a 115 V, 1/50 hp motor M. A wire W suspending the Q winds up or down on shaft of the motor depending upon the direction of rotation. There is also a manual switch in the controller to reverse the direction of the rotation at the end of a test.

The transducer T is connected to a cylinder L and the gas volume measuring column through the glass sensor tube E (Fig. 1). To take into account the variation in the reference pressure due to changes in the room temperature, a manometer M is provided. The difference between the changes in the pressure indicated by the manometer and the change in the barometric pressure would be the variation in the reference pressure due to room temperature fluctuations. M can be avoided if the cylinder and the transducer are kept in the constant temperature bath.

On dissolution of gas in the solution, the pressure in the system goes below the reference pressure, and this generates a proportionate electrical signal in the transducer. This energizes the motor speed control, the motor starts and raises the mercury reservoir till the pressure in both arms of the transducer is equalized. This sequence of operation

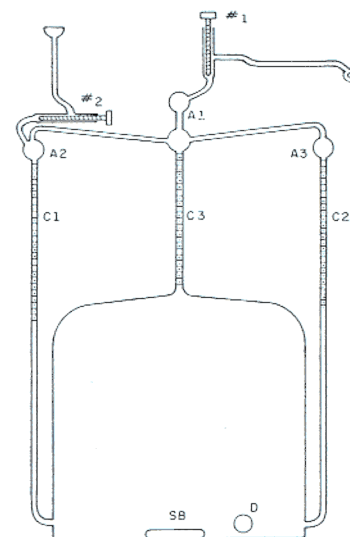


FIG. 2. Modified absorption cell.

continues till the equilibrium is attained. The response of the speed control is at a pressure difference of 2 cm of water gauge. If necessary, a better response can be obtained by using more sensitive transducers that are available commercially.

To avoid the overflow of mercury from the main mercury column, a microswitch S is inserted between the power supply and the magnetic stirrer Z and N through a multi-connection box X (see Fig. 4). The power supply is on when the microswitch is in the open position. The controlling arm of the microswitch as shown in Fig. 3 is connected with a wire loop to a ring Y. On the upper side of the ring, a hook U is attached to W. The length of the wire loop is adjusted so that when the mercury level in the gas volume measuring column crosses the uppermost graduated mark, U pulls down Y closing the microswitch. The system remains inoperative until the microswitch is manually adjusted to the open position. Before adjusting however, the direction of rotation of the motor is reversed and the stirrer is switched off.

An auxiliary switch S1 shown in Fig. 4 allows the operation of the motor independent of the pressure differential transducer. This was found necessary since any final residual indicator deflection that is not sufficient to start the motor could not be taken into account otherwise.

Due to the higher sensitivity of the transducer, a slight rise in the atmospheric pressure can raise or lower the mercury in the measuring column and cause errors in the

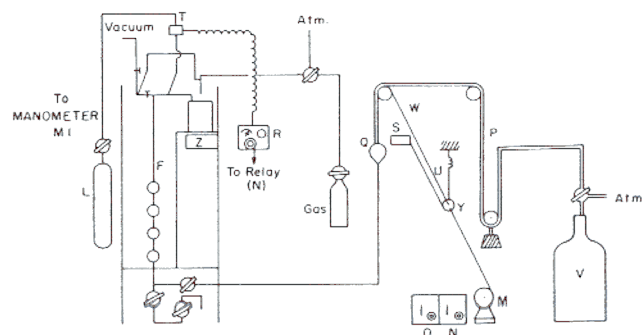


FIG. 3. Schematic diagram of the pressure control system.

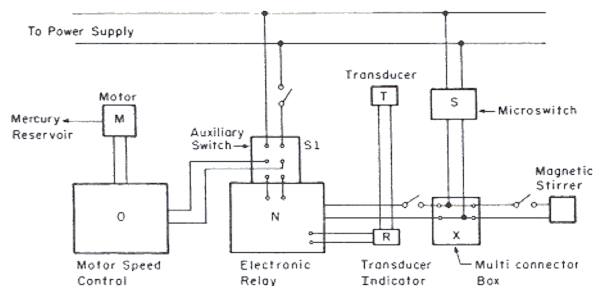


FIG. 4. Circuit diagram of the pressure control system.

solubility results. To reduce this problem, the open end of the mercury reservoir is connected to a 20 liter bottle, V, (see Fig. 3) and at the start of the experiment, the air in the reference arm of the transducer and that over the mercury in the reservoir is isolated from the atmosphere.

The constant temperature bath  $113 \times 38 \times 30$  cm is made of Plexiglas. The magnetic stirrer is outside the bath which makes it easy to mount the stirrer. To presaturate the incoming gas with the solution vapors a sparger J1 shown in Fig. 1 is provided. The temperature of the bath is controlled within  $\pm 0.1^\circ\text{C}$ .

## GAS DISSOLUTION

The test solution or solvent is first degassed in a cylinder G with an aspirator and a mechanical pump for a couple of hours (see Fig. 5). Completion of degassing in the cylinder is indicated by the absence of evolution of the air bubbles on the Teflon coated stirring bar. The solution is then transferred very slowly into the absorption cell by opening the two needle valves (No. 2, No. 2') till the cell is about 90% full. The solution in the cell is degassed with gentle stirring for about half an hour. The cell is then filled to slightly more than its calibrated capacity. The needle valve No. 2 is now closed and final degassing is done for about 2 h. If during

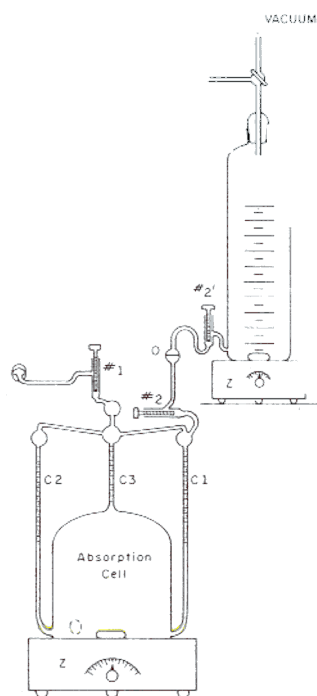


FIG. 5. Diagram illustrating the degassing arrangement.

TABLE I. Solubilities of methane and butane in triple distilled water at  $25^\circ\text{C}$  (unit: ml at STP/1000 g of water).

Gas	Present study	Claussen and Polglase <sup>3</sup>	Wen and Hung <sup>7</sup>	Morrison <sup>4</sup>
Methane	31.67	31.8	31.35	30.14
Butane	26.00	25.87	26.34 *	25.88

this period the solution level goes below the calibrated marks, more solution is transferred into the cell and degassing steps are repeated. This process is continued till complete degassing is achieved and the solution level in the absorption cell is within the desired range. At this stage the needle valve No. 1 is closed (Fig. 5) and the liquid levels in the three tubes C1, C2, C3 are read to determine the volume of the solution. The cell is now transferred into the constant temperature bath and connected to glass tube E (Fig. 1) containing the transducer probe. The mercury level in the measuring column is brought to the bottom glass bulb and all the stopcocks and needle valves are closed. At this point the transducer ports are connected to the atmosphere only. The system is evacuated and purged with the gas presaturated with solution vapors. It should be noted that the cell is at no time connected to the system when the gas is being purged. However, if there is any gas evolution during stirring of the solution in the cell, needle valve No. 1 is opened and the solution is further degassed. The system is then filled with gas and the mercury level in the central column is adjusted for the expected dissolution volume of the gas. The system is left undisturbed in this condition for 30 min. during which time the gas adsorption on the glass walls is complete. After adjusting the system pressure to that of the atmospheric pressure, stirring is started at a predetermined rate such that the solution is pumped up through the two outer capillaries C1 and C2 and sucked in through C3. After about 95% of expected gas dissolution the stirring rate is reduced to avoid supersaturation and is stopped when no further dissolution is indicated. The final residual deflection in the transducer indicator is nullified by raising or lowering the mercury reservoir and the mercury level in the central column is read to obtain the dissolution volume.

## RESULTS AND DISCUSSION

To test the reproducibility of the system, solubility of 99.9% pure methane and butane (purchased from Matheson Company) was determined in triple distilled water with a specific conductivity of about  $1.5 \times 10^{-6}$  mho/cm at  $25^\circ\text{C}$ . The results are compared with those of previous investigators in Table I. The maximum error in the present results is of the order of  $\pm 0.4\%$ . Results have also been obtained for solubility of methane and butane in sodium dodecylsulfonate solutions. This is discussed elsewhere.<sup>9</sup>

The major source of error in the present case is the variation in the bath temperature. This error can, however, be minimized by insulating the bath. Also the expansion of the solvent during gas dissolution has been neglected for computing the total solution volume. This can constitute another source of error though very small in the present range. For more accurate results a volume correction<sup>6</sup> should be made.

Further modifications to keep the reference pressure constant will result in the same partial pressure of the dissolving gas during all the experiments, and this would cause a further increase in the reproducibility of the results.

The major advantage of the present absorption apparatus is that it can be used without continuous personal attention and, therefore, can be used for prolonged experimentation. The apparatus can also be used for studying the kinetics of aqueous reactions where one reaction constituent is in the gaseous phase. The system can also be used to measure solubilities of gases in suspensions and thus to determine their adsorption at the solid-solution interface.

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