

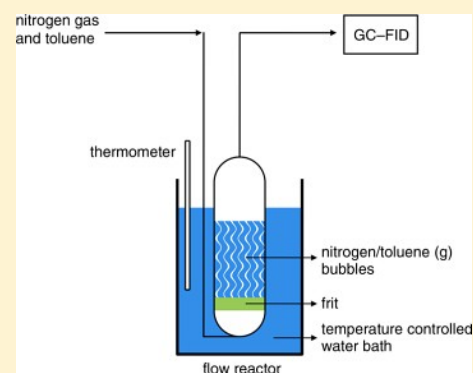
# A Laboratory Experiment To Measure Henry's Law Constants of Volatile Organic Compounds with a Bubble Column and a Gas Chromatography Flame Ionization Detector (GC-FID)

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## S Supporting Information

**ABSTRACT:** An undergraduate laboratory experiment is described to measure Henry's law constants of organic compounds using a bubble column and gas chromatography flame ionization detector (GC-FID). This experiment is designed for upper-division undergraduate laboratory courses and can be implemented in conjunction with physical chemistry, analytical chemistry, environmental chemistry, and toxicology laboratory courses. This experiment can be used to determine solubilities of organic compounds that have important implications in atmospheric chemistry and water pollution and build a useful database through undergraduate experiments.



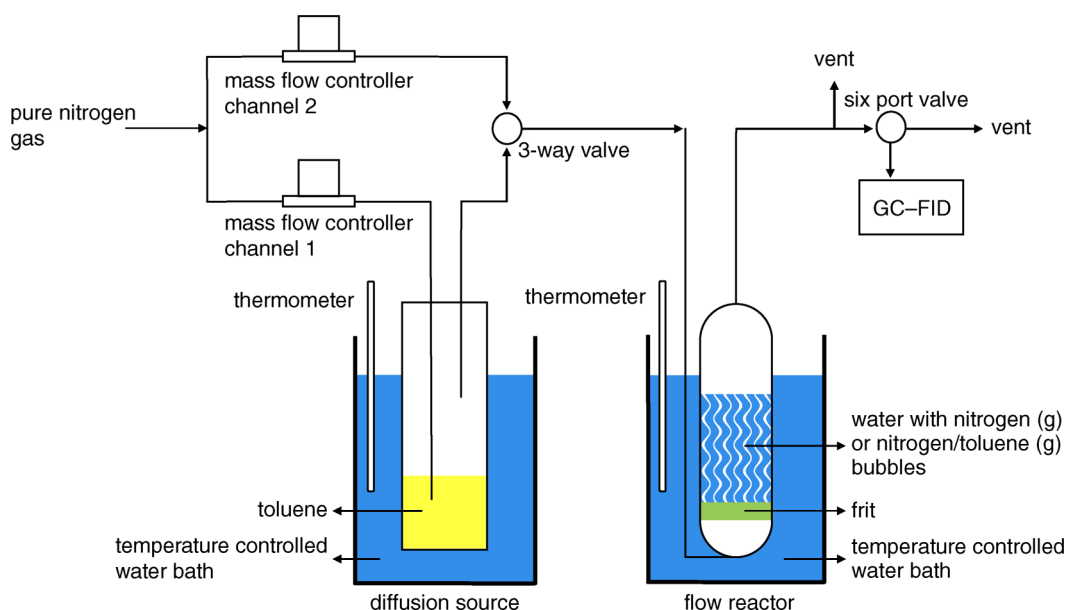
**KEYWORDS:** Upper-Division Undergraduate, Analytical Chemistry, Environmental Chemistry, Physical Chemistry, Hands-On Learning/Manipulatives, Atmospheric Chemistry, Equilibrium, Thermodynamics

Henry's law constant represents the solubility of a solute in a solution. There are thousands of different volatile organic compounds (VOCs) in the atmosphere and these VOCs can directly participate in the production of ozone and secondary aerosol particles and in turn affect climate, air quality, visibility, and human health. Whether a VOC can participate in gas-to-particle conversion processes is dependent on its solubility and other chemical and physical properties. Temperature dependence of solubility also determines the seasonal and altitude dependence of the gas-to-particle partition of VOCs. Solubility is one of the key parameters that determine the potential of toxic gas-phase contaminants to pollute water. Solubility also determines potential health effects of a toxicant. However, Henry's law constants of many organic compounds, including those closely relevant to environmental sciences, have not been measured directly but were estimated from thermodynamics data. The temperature dependence data of Henry's law constants are also lacking.<sup>1,2</sup>

There are several methods used to measure Henry's law constants, including the static and dynamic equilibrium methods.<sup>2</sup> In the static equilibrium method, steady-state equilibrium of the solute is reached between the gas and aqueous phases in an enclosed system. By measuring the relative concentrations of the solute in the gas and liquid phases, Henry's law constants are directly derived. If there is no equilibrium, this method can produce errors in the measured Henry's law constants. In the dynamic equilibrium method, the

solute of interest rises from the bottom of the column containing the liquid solution. After the thermodynamic equilibrium is reached between the gas (in the headspace) and the aqueous phases, the decay of gas phase concentrations of the solute is monitored. This method requires only the relative concentrations of the solute in the gas phase decaying with time. It is also important to ensure that equilibrium is established between the rising bubbles and the surrounding solution. This can be achieved by increasing the residence time of the bubbles in the liquid using a lower flow rate and longer column height. One of the advantages of the dynamic method over the static method is that both the Henry's law constant and the hydrolysis loss rate can be measured.

Previously, undergraduate laboratory measurements of Henry's law constants were typically based on the static equilibrium method.<sup>3–6</sup> Here, we describe an undergraduate laboratory experiment to determine the Henry's law constants of volatile organic compounds with the dynamic equilibrium method using a bubble column coupled with gas chromatography flame ionization detector (GC-FID). The bubble column method has been used for the measurement of Henry's law constants and hydrolysis loss rates of several VOCs relevant to the atmosphere.<sup>7,8</sup> We have implemented this experiment in an upper-level analytical chemistry laboratory course to measure

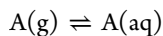


**Figure 1.** The experimental setup used to measure the Henry's law constant of a VOC in water using a bubble column and GC-FID. This figure shows the experimental setup for toluene, but this can be used for other compounds, such as benzene nitrile, which is shown in the present study. The detailed experimental conditions with regard to the flow rates and the volume of water, for toluene and nitrile benzene, are described in Experiments section.

the Henry's constant of toluene in water. Toluene was chosen because it is an air pollutant that has important implications in water pollution and in atmospheric chemistry by acting as an important precursor for secondary aerosol formation. The temperature dependence of the Henry's law constant of toluene is well established,<sup>1,2,9,10</sup> which also allows us to test and justify the concept of the experiment. To demonstrate the applicability of this method to other VOCs, we also present Henry's law constants of benzene nitrile. This is the first time, to our knowledge, that the measured Henry's law constants were reported for this VOC that plays important roles in atmospheric sciences and health effects.

## THEORETICAL BACKGROUND

Henry's law constants can represent a partitioning coefficient for a volatile compound between the gas and liquid phases. Consider the gas-to-liquid partitioning of a solute A:



For this case, the Henry's law constant  $H_{cc}$  (that is, the equilibrium constant) can be defined as

$$H_{cc} = \frac{C_{aq}}{C_g} \quad (1)$$

where  $C_{aq}$  and  $C_g$  are molar concentrations of the solute A in the aqueous and gas phases under the equilibrium condition. There are three assumptions in eq 1: (i) the solution is sufficiently dilute, (ii) the solute in the gas phase exhibits the ideal gas behavior, and (iii) chemical interactions between the solute and solvent are negligible.

In environmental chemistry, another form of Henry's law constant is often used,

$$H_{cp} = \frac{C_{aq}}{P} \quad (2)$$

where  $P$  is the partial pressure of the solute in the gas phase (atmosphere or atm). And,

$$H_{cc} = H_{cp}RT \quad (3)$$

where  $H_{cc}$  is unitless and  $H_{cp}$  is in  $\text{mol L}^{-1} \text{atm}^{-1}$ ,  $R$  is the ideal gas law constant ( $0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1}$ ), and  $T$  is the thermodynamic temperature (K). Thus, at  $25^\circ\text{C}$ ,  $H_{cc} = 24.46H_{cp}$ . There are various other forms of Henry's law constants with different units, and the detailed procedure of unit conversion of Henry's law constants is described elsewhere.<sup>2,11</sup>

On the basis of van't Hoff equation, the temperature dependence of the Henry's law constant can be expressed as

$$\ln H_{cc} = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad (4)$$

where  $\Delta H$  is the molar enthalpy of solvation of the solute ( $\text{J mol}^{-1}$ ),  $\Delta S$  is the molar entropy of solvation ( $\text{J mol}^{-1} \text{K}^{-1}$ ), and  $R$  is the ideal gas law constant ( $8.31 \text{ J K}^{-1} \text{ mol}^{-1}$ ).

In the dynamic equilibrium method as used in the present study, after the equilibrium has reached, the solute concentration in the gas phase,  $C_g$  (for simplicity, we denote  $C_g$  as  $C$  hereinafter), will decay with time ( $t$ ) due to solvation, in the following manner:<sup>12</sup>

$$-\frac{dC}{dt} = \frac{C\Phi}{H_{cc}V} \quad (5)$$

where  $\Phi$  is the gas volume flow rate at ambient pressure, and  $V$  is the liquid volume. By converting  $H_{cc}$  to  $H_{cp}$  using eq 3, eq 5 becomes

$$-\frac{dC}{dt} = \frac{C\Phi}{H_{cp}RTV} \quad (6)$$

In addition to the solvation process, the gas-phase solute is also lost with a first-order hydrolysis loss rate,  $k$  ( $\text{s}^{-1}$ ):

$$-\frac{dC}{dt} = kC \quad (7)$$

Combining eqs 6 and 7, the solute in the gas phase will decay as the following:

$$-\frac{dC}{dt} = \frac{C\Phi}{H_{cp}RTV} + kC \quad (8)$$

Solving eq 8 will lead to

$$\ln \frac{C_0}{C_t} = \left[ \frac{\Phi}{H_{cp}RTV} + k \right] t \quad (9)$$

where  $C_0$  and  $C_t$  are the concentration of the solute in the gas phase at equilibrium and that at time of  $t$  after the equilibrium at a specific temperature, respectively.

## EXPERIMENTS

The experimental setup in this experiment consisted of toluene solution, a fritted bubble column, and a GC-FID for the detection of toluene vapor (Figure 1). A toluene solution was used to add toluene to the nitrogen flow. The flow of the nitrogen gas containing toluene then passed through the bubble column to allow the toluene to equilibrate between the gas phase and aqueous phases. Once the desired equilibrium was reached, toluene was removed from the gas flow and the pure nitrogen gas stripped the toluene from the solution in the bubble column. The rate of removal of toluene in the headspace depends on the Henry's law constant, the flow rate of the nitrogen gas, and the volume of the aqueous solution in the column (eq 8).

In these experiments, typically the pure nitrogen gas with a flow rate of 50 standard cubic centimeters per minute (SCCM) was bubbled through the toluene solution (Figure 1). The output flow was merged with another flow of the pure nitrogen gas (700 SCCM). A 3-way valve was used to allow the flow from the toluene solution to be switched in and out of the system without affecting the main flow and the pressure in the system. The merged main flow then bubbled through from the fritted bottom of the bubble column (frit diameter 6 mm) containing 600 mL of deionized water. The entire system was under atmospheric pressure.

The toluene concentration in the headspace were monitored with a Hewlett-Packard 5890 GC (Palo Alto, CA) coupled with a FID. We used a 30 m long, 0.53 mm i.d., 1  $\mu$ m stationary phase thickness polyethylene glycol Stabilwax column (catalog # 10655, Restek Corporation, Bellefonte, PA) with a flow rate of 3 mL min<sup>-1</sup>. The injector was controlled with a six-port sampling-switching valve and a two-position actuator (VIGI Valco instruments, Houston, TX). FID signals (either peak height or area; the area should be linearly proportional to the peak height if the peak has a symmetric shape) were recorded as function of time. These FID signals (which are proportional to gas phase toluene concentrations in the headspace) were used to derive the Henry's law constant. Obtaining similar peak heights from successive injections signified that saturation was achieved. Experiments were performed under various nitrogen purging flow rates ( $\Phi$ ) flowing through the column ranging between 500 and 800 SCCM with an increment of 100 SCCM at each temperature of the water solution. Using the same experiment procedure, Henry's law constants were measured at four different temperatures (283, 288, 293, and 298 K).

For benzene nitrile, the same experimental setup and conditions used for toluene were employed, except that nitrogen purging flow rates ( $\Phi$ ) were 700, 1000, 1300, and 1600 SCCM and the water volume ( $V$ ) was 80 mL. These  $\Phi$  and  $V$  conditions (that is,  $\Phi/V$  ratios) were chosen to accommodate a higher solubility of this compound (eq 5).

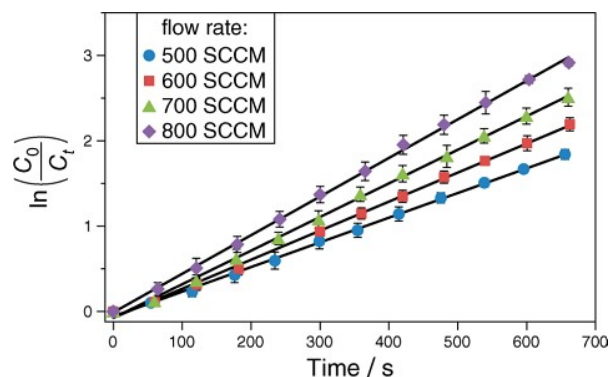
This experiment is applicable to a small group (2–3) of students. The experiment to obtain the Henry's law constant for a specific temperature takes between 2 and 3 h. Each group can conduct the experiment for one temperature using the same experimental setup on different days, and several groups of students can share the data to determine the temperature dependence.

## HAZARDS

Toluene is a flammable liquid, is harmful or fatal if swallowed, and causes irritation to skin, eyes, and respiratory tract. Refer to the Material Safety Data Sheet for toluene. Carefully control the pressure of nitrogen flowing through the mass flow meter controllers. Sudden increase in pressure may cause the system to explode.

## RESULTS AND DISCUSSION

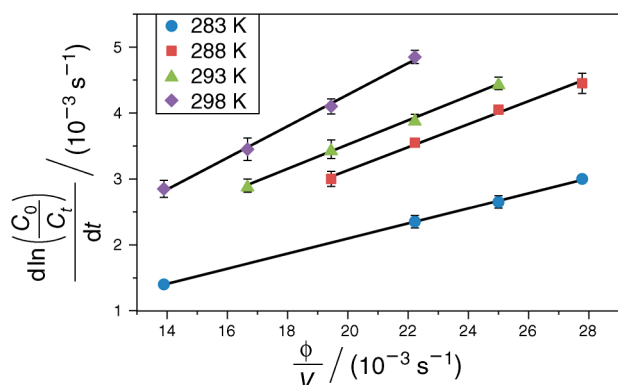
Figure 2 shows the  $\ln(C_0/C_t)$  versus  $t$  plots taken at 293 K with different  $\Phi/V$  values. Using the slopes of the plots [that is,  $d$



**Figure 2.** The measured  $\ln(C_0/C_t)$  vs time for the toluene/water system at 293 K for  $\Phi$  from 500 to 800 SCCM with  $V$  of 600 mL. Each data point represents the median value derived from 4 sets of experiments made under the same experimental conditions. The vertical bars indicate the 95% confidence level intervals.

$\ln(C_0/C_t)/dt$ ] under different  $\Phi$  conditions,  $d \ln(C_0/C_t)/dt$  versus  $\Phi/V$  plots were constructed (Figure 3). According to eq 9, the slope of Figure 3 corresponds to  $1/(H_{cp}RT)$  and the intercept corresponds to  $k$ . The measured Henry's law constant ( $H_{cp}$ ) and the first-order loss rate ( $k$ ) of toluene in water at temperatures ( $T$ ) from 283 to 298 K are shown in Table 1. Both  $H_{cp}$  and  $k$  are derived from four sets of experiments made under the same experimental conditions. One standard deviation values are also included in Table 1. The  $H_{cp}$  at 298 K was  $0.17 \pm 0.009$  mol L<sup>-1</sup> atm<sup>-1</sup> (with one standard deviation), consistent with literature values within the range from 0.13 to 0.21 mol L<sup>-1</sup> atm<sup>-1</sup>.<sup>9,10</sup> The hydrolysis loss rate ( $k$ ) was on the 10<sup>-4</sup> s<sup>-1</sup> order for temperatures from 283 to 298 K (Table 1), indicating that the hydrolysis loss of toluene is very low at these temperatures.

Using  $H_{cp}$  taken at various temperatures, the  $\ln H_{cc}$  versus  $1/T$  plots were constructed (Figure 4), and  $\Delta H$  and  $\Delta S$  were determined from the slope and intercept (eq 4). The derived

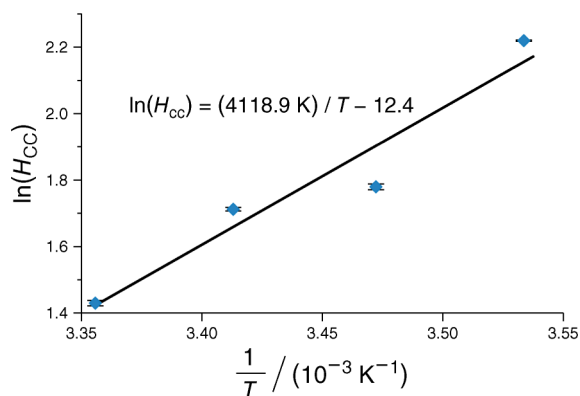


**Figure 3.** The  $d \ln(C_0/C_t)/dt$  vs  $\Phi/V$  for the toluene/water system at four different temperatures. Vertical bars indicate one standard deviation values.

**Table 1.** The Measured Henry's Law Constant ( $H_{cp}$ ) and the First-Order Loss Rate ( $k$ ) of Toluene in Water

T/K	$H_{cp}^a / (\text{mol L}^{-1} \text{atm}^{-1})$	$k^a / \text{s}^{-1}$
283	$0.38 \pm 0.002$	$0.0002 \pm 0.00005$
288	$0.24 \pm 0.009$	$0.0004 \pm 0.0002$
293	$0.23 \pm 0.005$	$0.0001 \pm 0.0002$
298	$0.17 \pm 0.009$	$0.0005 \pm 0.0001$

<sup>a</sup>Both  $H_{cp}$  and  $k$  are derived from four sets of experiments made under the same experimental conditions. One standard deviation values are also included.



**Figure 4.** The measured  $\ln H_{cc}$  vs  $1/T$  measured for the toluene/water system. Vertical bars indicate one standard deviation values.

$\Delta H$  was  $-34.2 \pm 6.6 \text{ kJ mol}^{-1}$  and the  $\Delta S$  was  $103.1 \pm 22.8 \text{ J mol}^{-1} \text{K}^{-1}$ . These measured  $\Delta H$  and  $\Delta S$  were fairly close to the molecular dynamics calculation results ( $\Delta H$  of  $-38.06 \text{ kJ mol}^{-1}$  and  $\Delta S$  of  $87.30 \text{ J mol}^{-1} \text{K}^{-1}$ ).<sup>13</sup>

Table 2 and Figure S1 (see the Supporting Information) show the measured  $H_{cp}$  of benzene nitrile at temperatures from 283 to 298 K. The  $H_{cp}$  was from 29.0 to 74.2  $\text{mol L}^{-1} \text{atm}^{-1}$  and the  $k$  was at the  $10^{-4} \text{ s}^{-1}$  range. The  $\Delta H$  was  $-40.3 \pm 2.7 \text{ kJ mol}^{-1}$  and the  $\Delta S$  was  $80.5 \pm 9.4 \text{ J mol}^{-1} \text{K}^{-1}$  (Figure S2). This is the first time that Henry's law constants were measured for this compound. These  $H_{cp}$ ,  $\Delta H$ , and  $\Delta S$  were also similar to those reported for other nitrile compounds (e.g., butyl nitrile  $H_{cp}$  from 27.6 – 69.5  $\text{mol L}^{-1} \text{atm}^{-1}$ ,  $\Delta H$   $-40.0 \text{ kJ mol}^{-1}$ , and  $\Delta S$   $75.3 \text{ J mol}^{-1} \text{K}^{-1}$ ).<sup>14</sup>

**Table 2.** The Measured Henry's Law Constant ( $H_{cp}$ ) and the First-Order Loss Rate ( $k$ ) of Benzene Nitrile in Water

T/K	$H_{cp}^a / (\text{mol L}^{-1} \text{atm}^{-1})$	$k^a / \text{s}^{-1}$
283	$74.2 \pm 1.99$	$0.00006 \pm 0.000002$
288	$52.9 \pm 0.67$	$0.00007 \pm 0.000003$
293	$42.0 \pm 0.64$	$0.00007 \pm 0.000009$
298	$29.0 \pm 0.82$	$0.00007 \pm 0.000005$

<sup>a</sup>Both  $H_{cp}$  and  $k$  are derived from four sets of experiments made under the same experimental conditions. One standard deviation values are also included.

## CONCLUSIONS

The bubble column method coupled with GC-FID technique is a convenient method for determining the Henry's law constants of VOCs. With this experiment, students can obtain hands-on experiences of operating the GC-FID instrument and learn the data analysis method to derive Henry's law constants and the temperature dependence. With this interdisciplinary research module, students can learn the physical concept of Henry's law constant, enthalpy, and entropy from a straightforward experiment in the context of environmental processes. This method can be adopted for a large number of VOCs simply by changing the flow rate and the solution volume (eq 5) for different solubility VOCs, as demonstrated by our measurements of toluene and benzene nitrile (solubilities are different over two to 3 orders of magnitude). With this experiment, a useful database of Henry's law constants of VOCs relevant to environmental chemistry can be built through undergraduate experiments and research.

## ASSOCIATED CONTENT

### Supporting Information

Instructions to students and instructors. This material is available via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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