

Determining the Enthalpy of Vaporization of Salt Solutions Using the Cooling Effect of a Bubble Column Evaporator

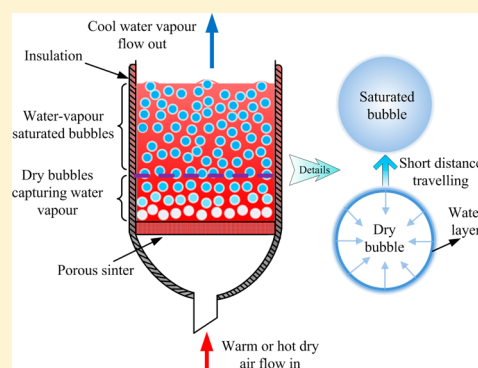
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Supporting Information

ABSTRACT: The enthalpy of vaporization (ΔH_{vap}) of salt solutions is not easily measured, as a certain quantity of pure water has to be evaporated from a solution, at constant composition, and at a fixed temperature and pressure; then the corresponding heat input has to be measured. However, a simple bubble column evaporator (BCE) was used as a novel method that allowed undergraduate students to determine the ΔH_{vap} value of a salt solution within an hour or so, because it only required temperature measurement (at a steady state) of the column solution and the inlet gas flowing into the column. In this article, by way of illustration, the ΔH_{vap} value of a 0.5 M NaCl solution was determined using the BCE process. In this experiment the evaporative cooling effects of the column were also easily demonstrated, as the inlet air at room temperature cooled the column solution to less than 10 °C. The change that students measured directly demonstrated the endothermic process of water vaporization. The role of several basic physical chemistry concepts, such as vapor pressure, phase transition, and enthalpy, involved in this experiment can be reinforced. An unexpected property of some common salt solutions, of bubble coalescence inhibition, was also observed in this experiment.

KEYWORDS: Upper-Division Undergraduate, Laboratory Instruction, Physical Chemistry, Hands-On Learning/Manipulatives, Aqueous Solution Chemistry, Phases/Phase Transitions/Diagrams, Physical Properties, Thermodynamics



Vaporization occurs with a phase change and heat transfer, which can be observed as a cooling effect in the residual solution. In this process, the enthalpy of vaporization (ΔH_{vap}) is the amount of heat required to vaporize any liquid from pure or solution form, at a constant temperature, pressure, and concentration. To measure this parameter for a solution, the amount of vaporized liquid must not significantly change the concentration of the solution, but there must be sufficient liquid to maintain the equilibrium vapor pressure at constant temperature. It is assumed here that the solute is completely involatile, for example, a common salt. The ΔH_{vap} values of salt solutions are not only important for many industries, such as in desalination and evaporative air conditioning, but it is also a fundamental thermodynamic property commonly taught in undergraduate courses in chemistry and physics.

Research has shown that undergraduate students often have problems understanding chemical thermodynamics and specifically the precise meaning of terms such as enthalpy.^{1,2} A simple laboratory experiment, through which students use enthalpy and enthalpy change to explain a readily observable phenomenon, can be an important mechanism to enhance their qualitative understanding of relevant concepts.¹ Usually, the teaching of enthalpy of vaporization is based on the use of measured vapor pressures in the Clausius–Clapeyron equation,^{3,4} and mostly for pure organic liquids and solutions.^{5–7} In this article, for the first time, a different approach was used and it presented a novel and simple laboratory experiment to

determine the ΔH_{vap} values of salt solutions by measuring simple, steady-state temperatures, which was directly related to evaporative cooling. This approach is particularly informative for undergraduate chemistry and physics students.

Theoretically, ΔH_{vap} values can be estimated using the Clausius–Clapeyron equation (eq 1), if there are vapor pressure values available at suitable temperatures:

$$P_2 = P_1 \times \exp\left[\frac{\Delta H_{\text{vap}}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right] \quad (1)$$

where P_1 and P_2 are the saturated vapor pressures at T_1 and T_2 ; R is the universal gas constant. In practice, these temperatures must not be too different, typically no more than 5 °C apart, since derivation of this equation is based on the assumption that ΔH_{vap} is constant over this temperature range. ΔH_{vap} values can also be calculated using related heat capacities based on Hess's law,⁸ but there are few published heat-capacity values for salt solutions. The good agreement reported⁹ for calculated ΔH_{vap} values of salt solutions using the Clausius–Clapeyron equation with other literature values suggests that this equation offers a valid method to obtain reliable ΔH_{vap} values.

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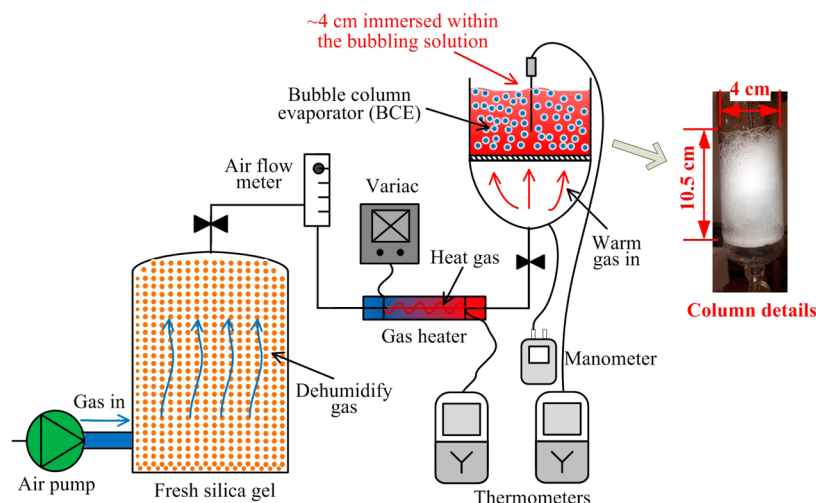


Figure 1. Schematic diagram of the BCE system and the column details.

In the literature, experimental measurements of ΔH_{vap} values of salt solutions often show large errors^{10–12} probably due to the effect of environmental conditions or due to the complexity of the experimental system used¹¹ or because it was measured at the salt solutions' boiling point.^{10,12} In recent work,^{9,13,14} a simple and novel system using a bubble column evaporator (BCE) was used to accurately and precisely determine the ΔH_{vap} of salt solutions at low temperatures, say less than 50 °C.

In the BCE process, uniform dry bubbles of 1–3 mm diameter were created through a porous glass sinter at the bottom of a glass column. These fine bubbles were inhibited from coalescence with each other, due to some unexpected effects,^{15,16} in some types of common salt solutions, which allowed the formation of a high density of small bubbles produced in the column by pumping dry inlet air, as shown in the schematic diagram of graphical abstract. This size of bubbles can be saturated by the water vapor within a few tenths of a second.¹⁷ The rapid vapor transfer and high density of small bubbles can be used as a basis for a novel approach to measure the ΔH_{vap} values of concentrated salt solutions.^{8,9,13,14}

The ΔH_{vap} measurements are based on the steady state conditions produced in the bubble column. Once the solution temperature at the top of the column reaches a steady state value, all the heat supplied by the dry bubbles entering the column will be used to evaporate the water. In other words, assuming no heat transfer with the environment, the heat provided by the bubbles (between entering and leaving the solution) exactly equals the enthalpy of vaporization required to reach equilibrium water vapor pressure within these bubbles. This energy balance in the bubble column is given by the following equation:^{8,9,13,14}

$$[\Delta T \times C_p(T_e)] + \Delta P = \rho_v(T_e) \times \Delta H_{\text{vap}}(T_e) \quad (\text{in } \text{J} \cdot \text{m}^{-3}) \quad (2)$$

where $C_p(T_e)$ is the specific heat of the gas (per unit volume) flowing into the bubble column at constant pressure; T_e is the steady-state temperature near the top of the column; $\rho_v(T_e)$ is the water-vapor density at T_e , which can be calculated from the water vapor pressure of salt solutions at T_e using the ideal gas equation; ΔT is the temperature difference in K between the gas entering and leaving the column. ΔP is the differential pressure between the gas entering the sinter and atmospheric pressure at the top of the column. This term corresponds to the

mechanical work done on the column by the pump, per unit volume of inlet gas. In this model it is also assumed that this work is converted completely into heat, which is absorbed by the column. This component can be directly related to the work-heat conversion in Joule's original paddle wheel experiments in 1843.

At steady state, i.e., stable column temperature, a dynamic energy balance must be established within the BCE. The heat supplied by the warm/hot bubbles is given by the cooling of the bubbles, that is $C_p(T_e) \times \Delta T$, per unit volume; meanwhile, there is a pressure decrement through the column, and so the work done to the column will be given by ΔP (per unit volume). The energy supplied to the column, from bubbles and the differential pressure, must then be balanced by the thermal energy required to vaporize water, to saturate the bubbles, which is given by the vaporization energy per unit volume, $\rho_v \times \Delta H_{\text{vap}}$.

Based on this equation, the required parameters to determine ΔH_{vap} values are the inlet gas temperature, column top solution temperature, and the differential pressure. It should be noted that the differential pressure is a stable parameter during the bubbling process, which can be measured using a manometer. Due to the reduced surface area of larger bubbles, per unit volume, that were produced in pure water, a longer time is required to reach the steady state temperature.⁸

■ MATERIALS

NaCl with purity level of $\geq 99\%$ was purchased from Sigma-Aldrich. Ultrapure water from a Milli-Q water purification system was used to prepare the salt solutions. A HIBLOW air pump was used to provide inlet air in the BCE system. Dry silica gel purchased from Ajax Fine Chem was used in the containers as a desiccator to dehumidify the inlet gas. A flow meter ($0\text{--}15 \text{ L} \cdot \text{min}^{-1}$) was obtained from Brin's Oxygen Company to monitor the inlet gas flow rate. A Pyrex column of around 4 cm diameter was used as the evaporation column. A Control Company 4000 Traceable digital thermometer was used to measure the column top solution temperature. K-Flex foam insulation materials (with a thermal conductivity of $0.045 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ at the operating temperature of around 10 °C) were used.

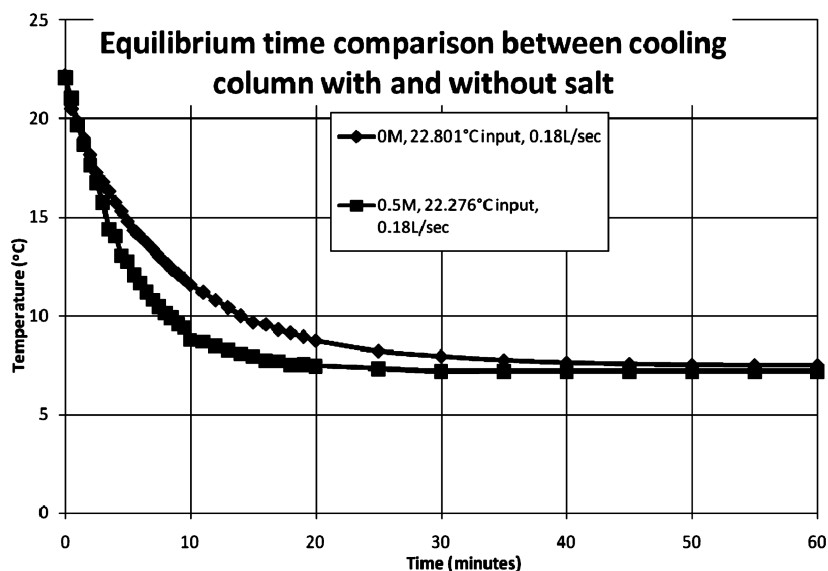


Figure 2. Column top solution temperature trend of 0.5 M NaCl and pure water with time using the BCE process (adapted from Francis and Pashley).⁸

EXPERIMENTAL PROCEDURE

The BCE process used here to obtain steady state conditions, and hence determine ΔH_{vap} values, is shown in Figure 1. The air was continuously produced from the air pump and dehumidified through the fresh silica gel. The dry inlet gas finally was sparged into the column solution and started bubbling. The column was clad with the insulation materials to prevent thermal transfer with the room conditions. An electrical gas heater can be used here for higher inlet-gas-temperature experiments, and so control the steady state temperature of the column solution.

After switching on the air pump, the flow rate was adjusted to around $10 \text{ L}\cdot\text{min}^{-1}$, to produce an appropriate bubble column density. Solution (70 mL) was poured into the column. Fine bubbles then started sparging into the solution, as shown in the column details in Figure 1. The temperature probe was then immediately immersed about 4 cm within the center of bubbling solution to record column solution temperature. A three-outlet valve can also be used before the column and connected with a manometer to measure ΔP values.

Once the column top solution temperature reached a steady state value, typically around $\pm 0.1 \text{ }^\circ\text{C}$, the experiment was ended and the recorded temperature data were analyzed for the cooling effect and used to calculate ΔH_{vap} values at this column temperature. Further experimental details, notes for the instructor, and a handout sample for students are given in the Supporting Information.

HAZARDS

The collapse of bubbles near the top column can splash some small solution drops out. They may go into the eyes or onto the skin when staying around the setup, which can cause irritation. So the proper laboratory clothing, gloves, and goggles must be used during the experiment operation. Flush eyes or hands with clean water for at least 15 min in the case of eye or skin contacts. The insulation materials must be used to clothe the air heater when it is used to increase the inlet air temperature, as the hot heater may cause skin burn if skin contacts.

CLASSROOM SETTING

This laboratory experiment was accomplished by an undergraduate physical chemistry class over about 2 h. There were about 10 students in the class and they were separated into 3 or 4 groups of 2–3 students. After the introduction of the experiment, each group of students made up the 0.5 M NaCl solution, set up the BCE process, and measured the temperatures during the experiment. They also did the calculations using the measured temperature data to determine the ΔH_{vap} value and then analyzed the accuracy of the BCE system, through comparison with literature data. The instructor prepared the necessary materials before the lab and provided the relevant literature data for students' calculation.

RESULTS AND DISCUSSION

Typical recorded column temperatures with time for 0.5 M NaCl solution and pure water are shown in Figure 2. The column solution cooled down to less than $10 \text{ }^\circ\text{C}$ by sparging dry inlet air at room temperature after around 10 min and reached a plateau value after around 30 min. This cooling process not only gives the students a basic understanding of quantitative endothermic vaporization, but also illustrates how evaporative air conditioners work.

Once the temperature reached the plateau value, the steady state temperature was used to determine the ΔH_{vap} value of 0.5 M NaCl, using eq 2, at that temperature. Some determined results are shown in Table 1, which also includes another experiment with a higher inlet gas temperature. The heat capacity of air and the vapor pressure of 0.5 M NaCl solution were obtained from ref 18 and ref 19, respectively.

Higher accuracy and precision for determining ΔH_{vap} values of various concentrated salt solutions can be obtained using more sophisticated equipment,¹⁴ including better insulation and automatic temperature recording. However, the simple BCE experiment shown here can be carried out as a simple and novel physicochemical laboratory for undergraduate students, giving reasonable agreement between determined and literature values.

The cooling effects produced by the BCE process can be further illustrated through the relationship between the inlet air

Table 1. Results from the BCE Experiments and the Comparison with Literature Values

Parameters	Experiment round 1	Experiment round 2
inlet air temperature (°C)	54.0	22.0
column top solution temperature (°C)	21.5	7.5
heat capacity of air (J·g ⁻¹ ·K ⁻¹)	1.005	1.006
water vapor density (mol·m ⁻³)	1.030	0.437
ΔP (Pa)	4128	1960
ΔH_{vap} based on energy balance (kJ·mol ⁻¹)	42.0	46.4
literature ΔH_{vap} (kJ·mol ⁻¹) ^a	44.2	44.7
error percent between experimental and literature ΔH_{vap} (%)	-4.9	+3.8

^aLiterature ΔH_{vap} values at different temperatures were generated from vapor pressure data¹⁹ using eq 1

temperature and the column top solution temperature, in this case for a 0.5 M NaCl solution, based on the prediction of eq 2 using the available vapor pressure values,^{19,20} as shown in Figure 3. This evaporative cooling effect has been observed for high inlet temperatures, up to 275 °C.²¹

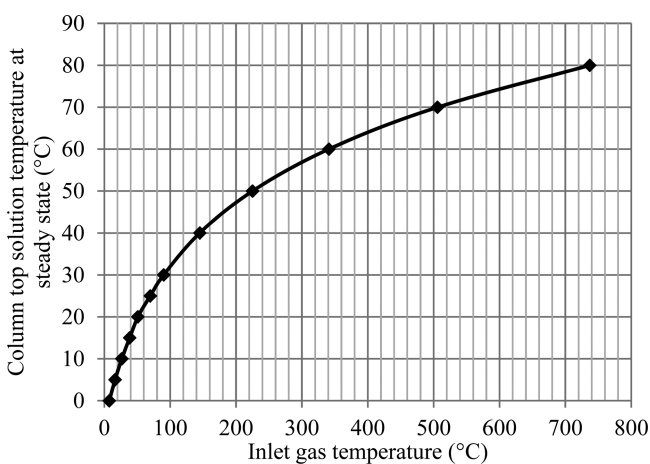


Figure 3. Predicted relationship between inlet gas temperatures and column top solution temperatures, at steady state, within a BCE containing 0.5 M NaCl solution.

CONCLUSIONS

This simple and novel experiment enabled students to have a better understanding of evaporative cooling used in commercial air conditioning units and in a semi-quantitative manner, as a method of measuring the ΔH_{vap} values of concentrated salt solutions. The experiment allowed them to deal with calculations which give reasonable ΔH_{vap} values, based on a simple theory, using easily obtained temperature data. Also, the rapid phase and thermal energy transfer involved in this simple experiment may stimulate students' curiosity regarding not only the basic science of bubble properties and salt solution properties, but also the practical applications of the BCE, such as for evaporative cooling and desalination.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available on the ACS Publications website at DOI: 10.1021/acs.jchemed.6b00314.

The materials for experiment setup, experimental procedures, the ΔH_{vap} calculation using experimental data based on the derived balance eq (eq 2), experimental handout for students, and notes for instructor (PDF, DOCX)

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Notes

The authors declare no competing financial interest.

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