

Identifying Liquid–Gas System Misconceptions and Addressing Them Using a Laboratory Exercise on Pressure–Temperature Diagrams of a Mixed Gas Involving Liquid–Vapor Equilibrium

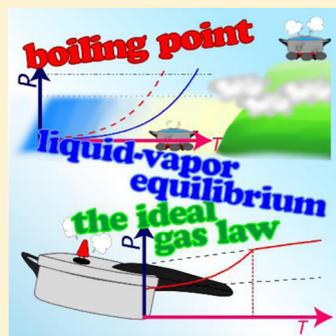
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Supporting Information

ABSTRACT: This study focuses on students' understandings of a liquid–gas system with liquid–vapor equilibrium in a closed system using a pressure–temperature (P – T) diagram. By administering three assessment questions concerning the P – T diagrams of liquid–gas systems to students at the beginning of undergraduate general chemistry course, lack of understanding of the fundamental concepts concerning liquid–vapor equilibria, the ideal gas law, and boiling points was identified. A learning program for liquid–gas systems was then designed for students at the undergraduate general chemistry level to address this issue. It consists of a laboratory experiment and postlaboratory exercise and is intended to provide integrated student understanding. During the learning program, students actively used the related concepts to explain the physical chemistry of a liquid–gas system and integrated the concepts to explain practical systems in their daily lives using a P – T diagram. An outline of the learning program is reported on the basis of our educational practice.

KEYWORDS: Second-Year Undergraduate, Laboratory Instruction, Physical Chemistry, Misconceptions/Discrepant Events, Gases, Phases/Phase Transitions/Diagrams, Thermodynamics



An understanding of liquid–vapor equilibria is essential for scientifically explaining various phenomena observed in daily life, the laboratory, and Earth's environment, but conceptual difficulties associated with the learning of this topic have been suggested by many educational researchers at different levels of chemistry teaching/learning.^{1–6} Recently, through written assessment questions administered to undergraduate students at the post general chemistry and physics level, Boudreaux and Campbell⁶ investigated the factors contributing to the conceptual and reasoning difficulties associated with learning about liquid–vapor equilibria in one-component closed systems. They found that phenomenological understandings of vaporization (condensation), vapor pressure, and liquid–vapor equilibria were limited, even for students who had learned these topics in high school and general chemistry courses at universities. Various misconceptions^{1–6} involving the incorrect application of the ideal gas law to the gaseous phase in a liquid–vapor equilibrium system⁶ were suggested as factors contributing to the students' confusion and limited comprehension of liquid–vapor equilibria. Therefore, these results obtained by Boudreaux and Campbell⁶ indicate that students should be provided opportunities for considering gas systems that experience changes in the molar amount of vapor.

In addition, students' understandings also appear to be limited with respect to closed systems containing a volatile liquid at conditions above its normal boiling point. This is because the pressure dependence of the boiling point must also be considered. The dependence of the boiling point on pressure is another topic covered in high school and

introductory (preparatory) chemistry courses at universities in relation to the phase changes of materials using pressure–temperature (P – T) phase diagrams.⁷ The explanation of the changes in the pressure of a system over a temperature range covering the liquid–vapor equilibrium, boiling point, and gas phase requires an understanding of liquid–vapor equilibria and the gas law, as well as how they are related via the boiling point. Such understanding of the complex phenomena involved in the liquid and gas regions in the P – T diagram is fundamental for interpreting the real phenomena that occur in our surroundings, such as water vapor in the air in a pressure cooker or in the atmosphere. The phenomena in a pressure cooker or in the atmosphere are multicomponent closed or open systems, respectively, each involving a liquid–vapor equilibrium. In addition, further advanced studies on phase changes and liquid–vapor equilibria in chemical thermodynamics are meaningful only if they are based on a comprehensive understanding of the phenomenology.

The aim of the present study, therefore, was to enable students to comprehensively understand the phenomenological nature of liquid–gas systems as described in P – T diagrams through the investigation of the basic chemical thermodynamics of phase changes and liquid–vapor equilibria in undergraduate general chemistry courses at universities. Prior to the introduction of the concepts of chemical thermodynamics of phase changes and liquid–vapor equilibria, students' under-

standings of the phenomenological nature of the gas law, liquid–vapor equilibria, and the boiling point were investigated using three assessment questions. Specifically, students were requested to select the most appropriate P – T diagrams for three different systems: a mixed gas consisting of water vapor and an ideal gas, water vapor only, and an ideal gas only. Based on the level of the students' understandings of the P – T diagram in the liquid–gas region and their possible misconceptions, a guided inquiry learning program in the form of a laboratory exercise involving the measurement of the vapor pressure in the temperature region of the liquid–vapor equilibrium was designed. This program is intended to be an additional learning activity about the basic chemical thermodynamics of phase changes and liquid–vapor equilibria in general chemistry courses at universities, and it has been implemented at our university for two years.

Herein, the difficulties students have with understanding the relationship between liquid–vapor equilibria and the ideal gas law in connection with the boiling point are first discussed by reviewing the results of the student assessment questions. The necessary aspects of an effective learning program that will enable students to understand the phenomenological nature of liquid–gas systems and the thermodynamic basis are also described. An outline of the developed laboratory exercise with data analysis requirements and the postlaboratory exercise for the reinforcement of the key learning points are also included. The effectiveness of the laboratory activity is assessed through educational practices using the developed laboratory exercise.

STUDENTS' UNDERSTANDINGS

Assessment Questions

Figure 1 explains the settings for the three assessment questions. At a temperature higher than the normal boiling point of water, three different closed vessels containing (1) a mixture of an ideal gas and water vapor, (2) water vapor, and (3) the ideal gas were presented. The students were asked to select the most appropriate P – T diagrams from 5–9 options

for each system when cooled slowly and provide the reasons for their choices. The questionnaires are given in the Supporting Information. The three assessment questions are summarized as follows.

Q1. Condensation of Water Vapor in a Mixed Gas System (Figure 1 Q1). A mixture of an ideal gas and water vapor is contained in a 1.0 L closed vessel at 400 K. Each component has the same partial pressure of 0.5×10^5 Pa. The mixture is cooled to 273 K. The students are asked about the change in the total pressure with temperature.

Q2. Condensation of Water Vapor (Figure 1 Q2). Water vapor is contained in a 1.0 L closed vessel at 400 K and a pressure of 0.5×10^5 Pa. The water vapor is cooled to 273 K. The students are asked about the change in the vapor pressure with temperature.

Q3. Ideal Gas Law and Partial Pressure (Figure 1 Q3). A mixture of two ideal gases is contained in a closed 1.0 L vessel at 400 K. Each component has the same partial pressure of 0.5×10^5 Pa. The mixture is cooled to 273 K. The students are asked about the changes in the total pressure and partial pressure of one of the gases with temperature.

The appropriate P – T diagrams for each question are also shown in Figure 1. The three assessment questions were successively administered over 3 weeks in the order Q1–Q3 to over 100 students at the beginning of the undergraduate general chemistry course during a 2-year period, allowing 10 min for each question at the beginning of weekly classes. The students are taking preservice science teacher training courses at our university. It was confirmed before administering the assessment question Q1 that all of the students had taken high school chemistry courses involving the ideal gas law, phenomenology of phase equilibrium, and P – T phase diagram. The order of the assessment questions, Q1–Q3, from the hardest to easiest, was selected in order to identify the possible source of students' difficulty for answering Q1 without giving any previous hints.

Results and Analysis

Table 1 lists the distributions of the P – T diagrams chosen by the students. Analyses of the explanations for each question are summarized in Tables S1–S3. For assessment question Q1, the correct P – T diagram (d) was chosen by only 7.5% of students. Most students (79.4%) chose (f), which describes the condensation of water vapor initiated at 373 K. Because both of the P – T diagrams (d) and (f) describe the pressure change according to the ideal gas law at a temperature above the boiling point and the pressure decrease due to the condensation of water vapor at temperatures lower than the boiling point, it is thought that most students at least understood the pressure changes in both temperature regions at a certain phenomenological level. In the explanations for Q1, 49.5% of students indicated that pressure is determined by the ideal gas law in the temperature region above the boiling point of water, and 45.8% of students mentioned the decrease in the pressure according to the saturated vapor pressure curve of water in the temperature region below the boiling point of water. However, only 4.7% of students mentioned the pressure-dependent change in the boiling point. Difficulty in recalling the pressure-dependent change in the boiling point when considering a P – T diagram was also suggested by the fact that 76.6% of students mentioned that the boiling point of water is 373 K.

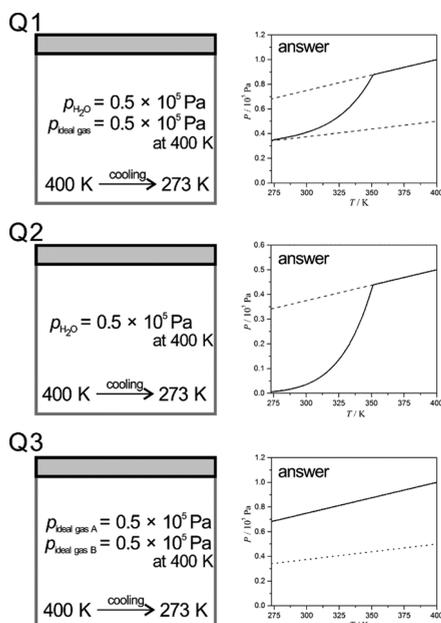


Figure 1. Schematic of the systems used in the assessment questions Q1–Q3 and the appropriate P – T diagrams for each system.

Table 1. Distribution of Student Responses to the P – T Diagram Multiple-Choice Question Options

Question (N)	Available Answer Options That Students Selected/% ^d								
	a	b	c	d	e	f	g	h	i
Q1 (107) ^a	0.0	3.7	0.9	7.5 ^e	8.4	79.4 ^f			
Q2 (111) ^b	0.0	2.7	46.8 ^f	9.0	0.0		1.8	1.8	37.8 ^e
Q3 (105) ^c	0.0	2.9	0.0	86.7 ^e	10.5				

^aQuestion 1 (Q1) had six options (five distractors) for selection, a–f. ^bQuestion 2 (Q2) had nine options (eight distractors) for selection, a–i. ^cQuestion 3 (Q3) had five options (four distractors) for selection, a–e. ^dSee the Supporting Information for the pressure–temperature diagram options for each question. ^eCorrect response. ^fIncorrect response that indicates the boiling point at 373 K.

For assessment question Q2 regarding the system containing only water vapor, the percentage of correct responses was increased to 37.8%. This improvement appears to be because of the fact that the system in Q2 was simpler than that in Q1. It is also thought that some students studied P – T diagrams of liquid–gas systems on their own in the week following the administration of assessment question Q1. This assumption is based on an increase in the number of students who mentioned the pressure dependence of the boiling point in their explanations (31.5%). Even then, 53.2% of students still mentioned a fixed boiling point of 373 K for water and selected the incorrect P – T diagram (c).

It can be clearly seen from the results of assessment question Q3 that the students' understandings of the ideal gas law and partial pressure were greater than that of the vapor pressure curve for a liquid–vapor equilibrium; the correct P – T diagram (d) was selected by 86.7% of the students. In addition, the correct descriptions of the ideal gas law and partial pressure were included in the explanations of 76.2% and 61.0% of the students, respectively. The lower percentage of students who correctly understood partial pressure was reflected by the portion of students (10.5%) who incorrectly chose P – T diagram (e), which indicates parallel lines for the total and partial pressures.

The results obtained for the assessment questions Q1–Q3 support the observations of Boudreaux and Campbell.⁶ At the level being promoted to undergraduate general chemistry courses, students understand the ideal gas law at the practical application level. On the other hand, their understanding of the saturated vapor pressure curve, and thus the concept of liquid–vapor equilibria, is at a phenomenological level because chemical thermodynamics using the Clausius–Clapeyron equation is required for physicochemical understanding. Such a difference in the level of understanding is a possible cause for the incorrect application of the ideal gas law to the saturated vapor pressure curve, which was discussed by Boudreaux and Campbell.⁶

In addition, as was observed by Boudreaux and Campbell,⁶ a significant portion of the students in the present study were confused about the pressure dependence of boiling point. The students correctly explained the mechanism of a pressure cooker and the difference in the boiling point of water in an open vessel on a beach and on the top of a high mountain⁸ because these topics are typically studied in high school chemistry and undergraduate introductory chemistry classes. However, their understanding of the relationship between the saturated vapor pressure curve and the ideal gas law for determination of the boiling point of a liquid in a closed system was largely lacking. The ideal gas law and the concept of liquid–vapor equilibria are often taught in different learning units or sections in high school chemistry and undergraduate introductory chemistry classes. The results of the present

assessment, however, suggest that these two concepts should be logically correlated in order for students to understand the boiling points of liquids in closed systems.

An informal survey of Japanese high school chemistry textbooks revealed that the concepts of boiling and boiling points are defined on the basis of a phenomenological model of liquid–vapor equilibria under atmospheric pressure. In some cases, the phenomenological concepts are extended to a closed system, for example, as exemplified by a decompression boiling experiment. However, in many textbooks, liquid–vapor equilibria and boiling are treated prior to discussion of the ideal gas law. It is thus apparent that comprehensive understanding of liquid–gas systems including liquid–vapor equilibria, boiling, and state changes in the gas phase is not necessarily achieved in high school chemistry classes in Japan if a comprehensive approach to liquid–gas systems is not reviewed after these different concepts are introduced.

Designing of a Learning Program for Undergraduate General Chemistry

In this situation, undergraduate general chemistry classes have the important roles of integrating these separated concepts related to liquid–gas systems, reinforcing the previously learned phenomenological concepts and introducing the physical chemistry of the system. The introduction of basic chemical thermodynamics of liquid–vapor equilibria in undergraduate general chemistry courses is one of the most promising opportunities for integrating these concepts. For this purpose, after the introduction of the Clausius–Clapeyron equation for the description of a liquid–vapor equilibrium in a one-component system, the application of the chemical thermodynamic relationship to a more complex mixed gas system involving a liquid–vapor equilibrium is required. This applied exercise gives students the opportunity to consider the relationship between liquid–vapor equilibria and the ideal gas law in connection with boiling points.

This realization stimulated our interest in developing a learning program composed of laboratory and postlaboratory exercises that would provide students with a better understanding of liquid–gas systems. In this laboratory exercise, students measure the change in pressure of a mixed gas involving a liquid–vapor equilibrium. The experimental data for the mixed gas system are separated into two components and analyzed using the Clausius–Clapeyron equation and the ideal gas law. In the postlaboratory exercise, the saturated vapor pressure curve is drawn using the data generated during the laboratory exercise along with reinforcement of the concept of liquid–vapor equilibria. Students are further requested to explain the pressure-dependent change in the boiling point of a liquid in open and closed systems using the P – T diagram. The learning program consists of a 3 h laboratory session and a 1 h post laboratory exercise using a PC. It has been applied to 9

student groups (3 members) in an optional laboratory class involved in an undergraduate general chemistry course following a lecture on the basic thermodynamics of liquid–vapor equilibria, as one of the laboratory exercises among those reported previously.^{9,10}

LABORATORY EXERCISE

Overview

To improve students' understandings of the temperature dependence of gaseous pressure involving a liquid–vapor equilibrium, an experiment that allows a comparison of the temperature-dependent changes in the pressures of an ideal gas system and a mixed gas system involving a liquid–vapor equilibrium via simultaneous measurement should be useful. For such an experiment, two pressure–temperature measurement vessels are prepared, one of which contains only air (reference vessel), while the other contains air and a selected liquid (sample vessel). Subjecting these two measurement vessels to the same temperature change, students simultaneously observe the different pressure changes in the two vessels with increasing temperature. The pressure in the reference vessel changes approximately according to the ideal gas law. In the sample vessel, the total pressure at a temperature can be interpreted as the sum of the partial pressures of air and the vapor generated from the liquid. Using the pressure–temperature curve for the reference vessel, the temperature dependence of vapor pressure can be obtained by subtracting the reference curve from the pressure–temperature curve for the sample vessel. The determined temperature dependence of vapor pressure is then thermodynamically analyzed using the Clausius–Clapeyron equation, as has been proposed in many previous laboratory exercises.^{11–14} By experimentally acquiring the data and performing the data analysis, students observe the temperature-dependent change in the pressures of the mixed gas with a liquid–vapor equilibrium and experience both the ideal gas law and the temperature dependence of vapor pressure in the form of a saturated vapor pressure curve.

Instrumental

The pressure–temperature measurement vessels used in the laboratory practice are shown in Figure 2. Twin measurement vessels are prepared using 100 mL glass bottles designed for sampling liquids for high-performance liquid chromatography.

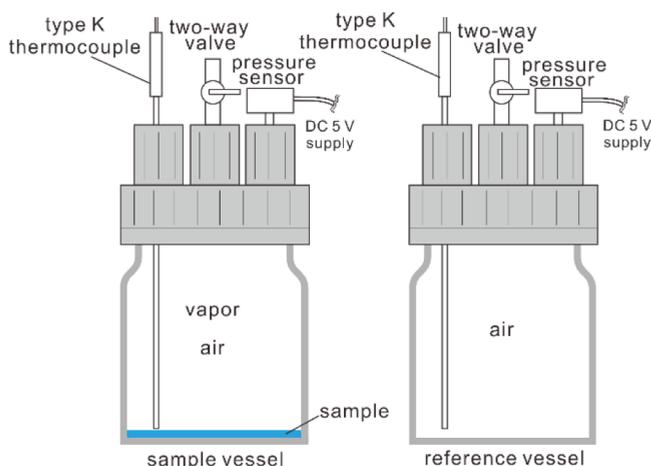


Figure 2. Schematic of the twin pressure–temperature measurement vessels.

Each vessel has a screw cap with three insert ports (1.6 mm in diameter \times 2, 6.0 mm in diameter \times 1) (Schott Duran). A sheathed thermocouple (KTO-16150, As One) and a differential pressure sensor (40PC015G1A, Honeywell) are inserted in the vessels through the 1.6 mm diameter ports of the screw caps, and a two-way valve (VXB1055, As One) is connected to the 6.0 mm diameter port using a plastic tube. The screw lids of the bottles and insert ports of the screw caps are carefully sealed using O-rings in order to avoid possible gas leaks. The pressure sensor is supplied with 5 V (direct current, dc) using an alternating current (ac)–dc converter (UN110-0520, UNIFIVE). Analog outputs from the two sheathed thermocouples and the two differential pressure sensors are recorded using a multichannel data logger (midi LOGGER GL200, GRAPHTEC), and the data acquisition is controlled using a PC.

Experimental Procedure

Distilled water or ethanol (99.5%) (2 mL) is transferred to the sample vessel. The content of the reference vessel is dry air. With the two-way valves on the screw caps left open, the twin measurement vessels are immersed in an electric water bath (WBS50, MASUDA). After stabilizing the temperature of the gas in the measurement vessels for approximately 10 min, the two-way valves for both measurement vessels are closed. The simultaneous acquisition of temperature–pressure data for the sample and reference vessels is initiated, and the starting temperature is determined after several minutes in order to record the offset voltage of the output from the differential pressure sensors. The water bath is then turned on, and measurements are continued. The temperature of the water bath is increased at a heating rate of approximately 1 °C min⁻¹ until it reaches 60 °C, at which point the experiment is halted.

HAZARDS

The electrical connections for the pressure sensors should be kept away from water. While handling ethanol, adequate ventilation is necessary and students are required to wear safety glasses and gloves.

ANALYSIS OF THE EXPERIMENTAL DATA

Vapor Pressure Curve and Temperature Dependence of the Partial Pressure of Air

Figure 3 shows typical experimental data for the pressure changes (ΔP) from the atmospheric pressure in the sample and reference vessels, which were reported by a student group. For both water (Figure 3a) and ethanol (Figure 3b), the change in the pressure with temperature in the sample vessel was greater than that in the reference vessel. A linear relationship between the temperature and ΔP is clearly seen for the pressure change in the reference vessel. Using the data for the reference vessel, students analyze the behavior according to the gas law by assuming an ideal gas.

$$P = \frac{nR}{V} \cdot T \quad (1)$$

where n , R , and V are the molar amount, the gas constant, and volume, respectively. When ΔP is plotted against T , the absolute value of the intercept corresponds to the atmospheric pressure (Figure 3c).

With respect to the pressure change in the sample vessel, students readily understand that the total pressure change equals the sum of the changes in the partial pressures of air and

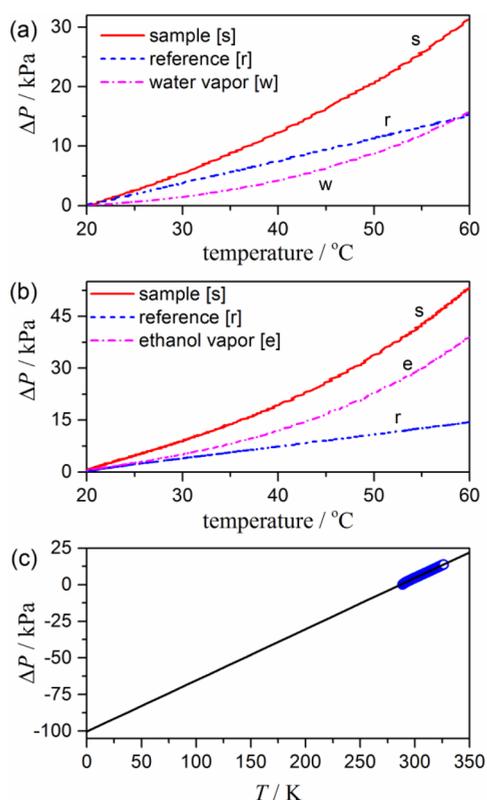


Figure 3. Typical experimental results for the temperature–pressure measurements and data analyses: (a) water, (b) ethanol, and (c) plot of ΔP versus T for the reference vessel.

the vapor. Based on this idea, the recorded pressure change in the reference vessel is subtracted from that for the sample vessel in order to obtain the vapor pressure curve, as shown in Figures 3a and 3b. The vapor pressure curve can be used for thermodynamic analysis.

Enthalpy of Vaporization: Application of the Clausius–Clapeyron equation

For students who have learned the thermodynamics of phase changes in an undergraduate general chemistry course, the analysis of the temperature dependence of the vapor pressure using the Clausius–Clapeyron equation is understood. For students who have not studied the topic, the thermodynamic relationship of the phase change can be actively understood by analyzing the experimental data. On a P – T phase diagram, the slope of the liquid–vapor equilibrium curve can be expressed by the Clapeyron equation:^{15,16}

$$\frac{dP_{\text{vap}}}{dT} = \frac{\Delta_{\text{vap}}H}{T\Delta_{\text{vap}}V_{\text{m}}} \quad (2)$$

where P_{vap} , T , $\Delta_{\text{vap}}H$, and $\Delta_{\text{vap}}V_{\text{m}}$ are the vapor pressure, absolute temperature, enthalpy of vaporization, and molar volume change due to vaporization, respectively. Assuming that $\Delta_{\text{vap}}H$ is a constant within the temperature range under investigation, the volume of liquid in the system is negligible, and the vapor behaves as an ideal gas, eq 2 can be integrated to give eq 3:

$$\ln P_{\text{vap}} = -\frac{\Delta_{\text{vap}}H}{R} \cdot \frac{1}{T} + C \quad (3)$$

where C is a constant value, that is, the intercept for the $\ln P_{\text{vap}}$ versus T^{-1} plot.

Figure 4 shows the results of the analysis of the experimental data (Figure 3) obtained using eq 3. The experimental data for

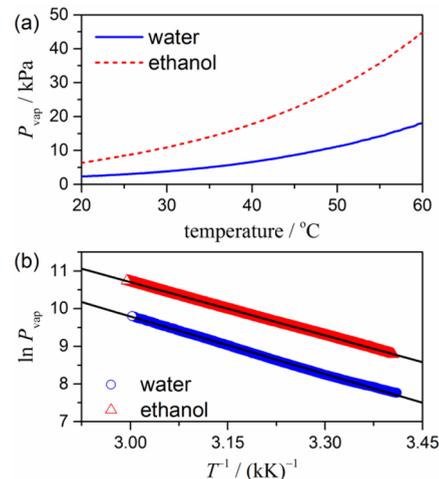


Figure 4. Typical results for the data analysis of experimentally derived vapor pressure–temperature curves: (a) vapor pressure–temperature curves and (b) $\ln P_{\text{vap}}$ versus T^{-1} plots.

ΔP versus T is modified to P_{vap} versus T by adding the initial vapor pressure at the start of the experiment (20°C), which is known from the literature (Figure 4a). The modified data are used to prepare the $\ln P_{\text{vap}}$ versus T^{-1} plot (Figure 4b), and the slope and intercept of the linear relationship are determined via the linear regression analysis. The enthalpy of vaporization in the measured temperature range calculated from the slopes of the linear regression lines in Figure 4b was 42.4 ± 0.1 and 39.7 ± 0.1 kJ mol^{-1} for the vaporization of water and ethanol, respectively. The enthalpy of vaporization reported by the different student groups ranged from 39.1 to 47.0 kJ mol^{-1} and 36.2 to 40.9 kJ mol^{-1} for the vaporization of water and ethanol, respectively. The values are nearly coincident with the values calculated using the vapor pressure data in the literature for the corresponding temperature range (20 – 60°C), which are 43.5 and 41.9 kJ mol^{-1} for water and ethanol, respectively.¹⁷

POSTLABORATORY EXERCISE

Using their experimental results, students investigate the relationship between the vapor pressure–temperature curve and the ideal gas law via the boiling point in the postlaboratory exercise. Figure 5 shows the steps included in the student exercises.

Simulation of the Saturated Vapor Pressure Curve

Using the results of the $\ln P_{\text{vap}}$ versus T^{-1} plot (Figure 4b) and assuming constant thermodynamic parameters within the temperature range of the calculation, the vapor pressure curve can be calculated using eq 4:

$$P_{\text{vap}} = \exp\left(-\frac{\Delta_{\text{vap}}H}{R} \cdot \frac{1}{T} + C\right) \quad (4)$$

Figure 5a shows the vapor pressure–temperature curves for water and ethanol calculated using the $\Delta_{\text{vap}}H$ and C values determined by a student group. After drawing the vapor pressure–temperature curves, students are asked to compare

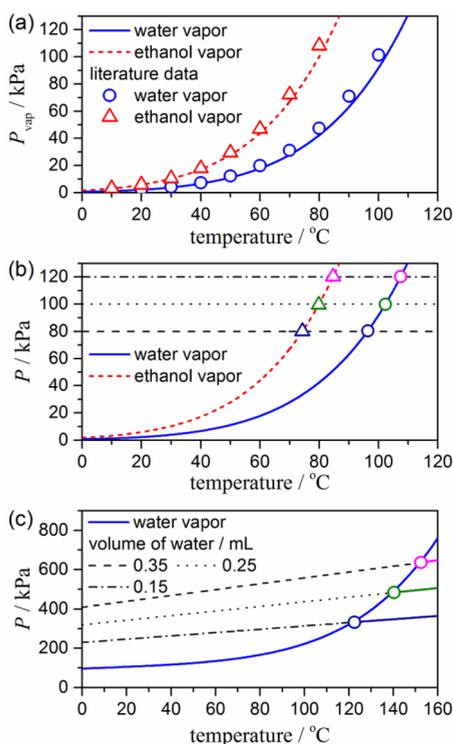


Figure 5. Steps in the postlaboratory exercise: (a) comparison of typical vapor pressure–temperature curves calculated using the results of the $\ln P_{\text{vap}}$ versus T^{-1} plots with literature data; (b) determination of the boiling point in an open system; and (c) determination of the boiling point and calculation of the change in the total pressure with temperature in a closed system of the mixed gas with a liquid–vapor equilibrium.

the vapor pressure–temperature curve with the literature data for the saturated vapor pressure at different temperatures (Figure 5a). Although some deviations in the calculated vapor pressure from the literature data are observed at temperatures higher than the measured temperature region, the correspondence is acceptable when considering the constant thermodynamic parameters of vaporization assumed for all temperature regions.

Here, an important concept of the saturated vapor pressure, namely, that the vapor pressure is determined only as a function of temperature, should be reinforced. The experimental conditions for the binary system consisting of water vapor and air are recalled to derive the independence of the vapor pressure from the total pressure. When asked for some practical examples, students mentioned gas lighters and portable gas stoves, for which the fire power is nearly constant at the beginning and end of use, but increases if warmed in the hand. Using this example, students discussed the physical nature of liquid–vapor equilibria.

Boiling Point in an Open System

Next, the relationship between the vapor pressure–temperature curve and the boiling point is reinforced for the students using the P – T diagram. Students' understandings of the different behavior in open and closed systems concerning the determination of the boiling point is not clearly separated when discussing the changes in the boiling point with altitude and the function of a pressure cooker. Therefore, the relationship should be discussed separately for open and closed systems in this postlaboratory exercise.

In an open system under constant atmospheric pressure, the boiling point is dependent on the atmospheric pressure. The difference in the boiling point of water on a beach and at the top of a high mountain is a well-known example of this phenomenon. Students are asked to explain this difference, which arises because the atmospheric pressure is different at different elevations, using the calculated vapor pressure curve. Students determine the boiling points of water and ethanol in an open system from the intersection point of the calculated vapor pressure curve and level lines drawn at different atmospheric pressures (Figure 5b).

Boiling Point in a Closed System

For discussion of the boiling point of a liquid in a closed system containing a mixed gas, students are required to integrate many fundamental concepts concerning liquid–vapor equilibria, the ideal gas law, and boiling points. The liquid–gas system in the sample vessel in the experiment (Figure 2) is assumed to contain water, water vapor, and air for this discussion. First, the students should consider the change in the total pressure with temperature by assuming that all of the substances in the system are in the gaseous state. The molar amount of air can be calculated using the ideal gas law from the slope of the ΔP versus T plot for the reference vessel (Figure 3c) and the volume of the vessel (141.1 mL, which is provided by the instructor). For different volumes of liquid water transferred to the sample vessel, for example, 0.15, 0.25, and 0.35 mL, the total molar amounts of each of the substances contained in the sample vessel are calculated as the sums of the molar amounts of air and the initially transferred water. Then, assuming that all of the substances are in the gaseous state and behave as ideal gases, the change in the total pressure with temperature under constant volume conditions is drawn using the ideal gas law, as shown by the dashed lines in Figure 5c. In addition, students should consider the change in the total pressure with temperature for a mixed gas with a liquid–vapor equilibrium. Under these conditions, the total pressure is the sum of the partial pressure of air and the vapor pressure. The change in the partial pressure of air with temperature under constant volume conditions is calculated using the ideal gas law using the amount of air calculated previously. The partial pressure of water vapor at different temperatures is illustrated by the calculated vapor pressure–temperature curve. The sum of the partial pressures of air and the water vapor is shown by the solid line in Figure 5c. The points where the solid and dashed lines intersect are the boiling points for each liquid–gas system containing different molar amounts of water molecules. Taking the lower pressure line from the solid and dashed lines at different temperatures, the change in the total pressure of the mixed gas with a liquid–vapor equilibrium is determined. During this investigation of a closed system, the students actively use the fundamental concepts concerning liquid–vapor equilibria, the ideal gas law, and boiling points and obtain the information needed to correctly answer assessment question Q1 (Figure 1).

Based on the results of the analyses assuming open and closed systems (Figures 5b and 5c), students are requested to explain the functioning of a pressure cooker.

EDUCATIONAL PRACTICE

The proposed learning program was practiced using the student handout provided in the Supporting Information. At the beginning of the learning program, the assessment question Q1

was administrated to the students. The results indicated practically the same trend with that revealed in the previous assessment in the general chemistry class. Based on the experimental setting of the measurement vessels (Figure 2), students were initially asked to propose the expected changes in total pressure in each measurement vessel with temperature. After instructions necessary for the data collection, students carried out the measurements according to the provided experimental procedures. Then the differences of the collected data for the respective measurement vessels were discussed in comparison with their preconception.

The data analyses and postlaboratory exercise were administrated in a strategically organized stepwise manner, aiming to enable the active learning using the previously learned knowledge and in an inquiry style to find the relationship between the ideal gas law and liquid–vapor equilibrium in connection with the boiling point (see Student Handout in the Supporting Information). In each step of data analysis, necessary discussions were introduced in each student group and in the class. For the data analysis, it was recommended to students to use a spreadsheet program in a PC, which is partially formatted without inputting the necessary functions for calculations. The Excel spreadsheet developed by the students during the data analysis was also provided in the Supporting Information with sample data. For the students who have not learned the basic thermodynamics of liquid–vapor equilibrium, a necessary instruction on the Clausius–Clapeyron equation was provided during the data analysis. Using the collected experimental data, students finally determined the reasonable values of $\Delta_{\text{vap}}H$.

The postlaboratory exercise was started from the drawing of the $P_{\text{vap}}-T$ curve for the liquid–vapor equilibrium using the experimentally determined thermodynamic parameters. Further considering the contribution of the ideal gas law to the $P-T$ diagram in an open and closed liquid–gas systems, students understood the boiling points of the liquid on the basis of the relationship between the ideal gas law and the liquid–vapor equilibrium. The revealed relationship was used to explain the relevant phenomena encountered in our daily life. In the laboratory report submitted by the students one week after the laboratory exercise, 100% of the students correctly described the phenomena assumed in Q1 and experienced in our daily life, effect of the elevation on the boiling point, and the functioning of a pressure cooker, based on physical chemistry.

CONCLUSIONS

Students' understandings of liquid–gas systems involving liquid–vapor equilibria are not necessarily integrated at the level being promoted to undergraduate general chemistry courses. The $P-T$ diagram of a liquid–gas system is a useful learning tool for reinforcing the fundamental concepts concerning such systems and integrating these concepts. The learning program developed in this study provides opportunities for investigating the fundamental concepts in a step-by-step manner and subsequently requires necessary integration of the concepts to draw the $P-T$ diagram for a closed liquid–gas system involving a liquid–vapor equilibrium. Consequently, students' understandings are elevated to the level required for explaining practical phenomena concerning liquid–gas systems using $P-T$ diagrams.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available on the ACS Publications website at DOI: 10.1021/acs.jchemed.5b00107.

Assessment questions; student handout; instructor information (PDF, DOCX)
Data analyses (XLSX)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The present work was supported by JSPS KAKENHI Grants 25242015, 25350202, 25350203, and 26350235.

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