

Determination of the Vapor Pressure Curve of a Liquid in the Presence of a Nonvolatile Solute

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Abstract: We present a modification of the data analysis for the classical physical chemistry experiment “Determination of Enthalpy of Vaporization by the Boiling-Point Method.” The vapor pressures of solutions of both ionic and molecular compounds are determined at different temperatures. In this experiment we show that the enthalpy of vaporization change is dependent on the type and amount of nonvolatile solute present. Sets of data collected for different concentrations of sodium chloride, urea, and sucrose solutions are analyzed in order to determine ΔH_{vap} and ΔS_{vap} for pure water and for solutions of ionic and molecular solutes.

Students perform the data analysis taking into consideration the activity coefficient for the solution and the mole fraction of the solvent. Simultaneous data analysis is introduced and results are used to explain the meaning of the physical parameters determined using this method of data analysis.

Introduction

Most chemistry textbooks list vapor-pressure lowering as one of the four colligative properties of solutions; thus, vapor pressure lowering is claimed to depend on the amount of solute, regardless of whether the solute is ionic or molecular [1–5]. Most of these references mention the requirement of ideality, and some state that there is a maximum molar concentration beyond which the rule no longer holds. In our experiment we observe most of the vapor-pressure lowering in solutions with lower concentration. If, in fact, most of the solute effect takes place during the initial stages of vaporization and if the change is minimum at higher solute concentration (as we suggest later), then the identity of the solute becomes as important as the molar concentration.

In this experiment we are studying two-phase equilibria, liquid–vapor, of pure water and aqueous solutions of nonvolatile solutes. Two-phase equilibria are a result of equal chemical potentials, which can be equated in an ideal approximation to the molar Gibbs free energy in the two phases. The thermodynamics of the vapor pressure in equilibrium with the liquid phase are monitored by applying the Clausius–Clapeyron equation. Raoult’s law is an expression of vapor-pressure lowering, as the number of solute molecules is increased, while the mole fraction of solvent is decreased.

Ideal solutions obey Raoult’s law and the vapor pressure of each component in the solution is proportional to its mole fraction (no factors are included for ionic species). In real solutions Raoult’s law can be applied only at very small concentrations of solute; deviations from Raoult’s law occur at higher concentrations. In nonideal solutions activity and activity coefficients are introduced into the calculations [6–9].

For nonideal solutions, the chemical potential for the solution with respect to component i is

$$\mu_i = \mu_i^\circ + RT \ln a_i$$

As X_i approaches 1 and the system approaches pure solvent, μ_i must approach μ_i° and $\ln a_i$ equals zero.

For an ideal solution $\mu_{\text{ideal}} = \mu_i^\circ + RT \ln X_i$

Thus,

$$\mu_i - \mu_{\text{ideal}} = \mu_i^\circ + RT \ln \frac{a_i}{X_i} = RT \ln \gamma_i$$

where γ_i is the activity coefficient and is a measure of the extent of deviation from ideal behavior [10–17].

In this experiment we are testing the validity of the dependency of vapor pressure-lowering, as a colligative property, on the number of molecules of solute present. The effect of ionic solutes and molecular solutes on the heat of vaporization are determined using the Clausius–Clapeyron equation.

Experimental Procedure

Materials, Chemicals, and Equipment. The apparatus for vapor-pressure determination is shown in Figure 1. The required reagents are distilled water, sodium chloride, urea, sucrose, and boiling chips.

Methods. Solvents or solutions under investigation are subjected to various measured pressures. The liquid (or solution) boiling temperature is determined at each of the pressures. The vapor pressure of the liquid is determined at the various temperatures at which the liquids boil. The procedure is as follows.

Construct the apparatus as shown in Figure 1. Obtain a 500-ml round-bottomed flask with a side sleeve for a thermometer. Place 250 ml of the liquid or solution whose vapor pressure is to be determined in the 500-ml flask with some boiling chips. Fit the top of the flask with a two-way adapter. Connect two water-cooled bulb-type condensers to the adapter. A vacuum line (or an aspirator) is attached to a vacuum trap (500-ml vacuum flask) that is attached to one of the condensers through a three-way valve, then to a pressure capacitance or mercury manometer. Turn on the water aspirator to evacuate the system to the lowest possible pressure that corresponds to the lowest boiling temperature of water. Use a heating mantle to heat the round-

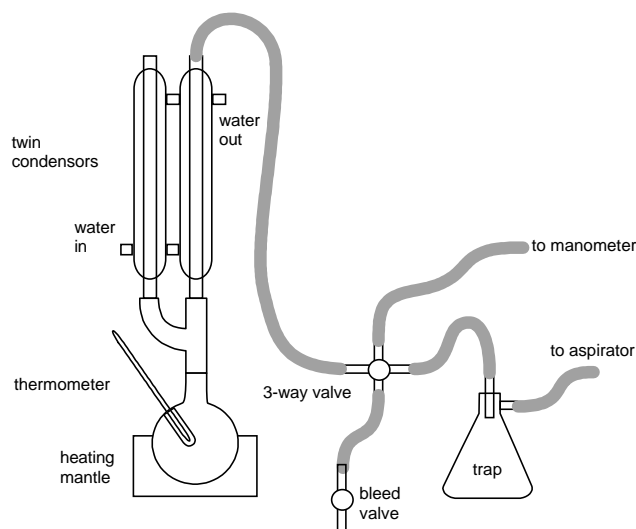


Figure 1. Apparatus for vapor-pressure determination.

bottomed flask until the liquid boils. Read the boiling-point temperature and the pressure. Open the pressure control valve to increase the pressure (by about 20–30 mm Hg) and obtain the new boiling point at the higher pressure. Repeat this procedure to obtain about ten data points over a range of pressures, the last reading being at atmospheric pressure.

Repeat the procedure above for the solutions of sodium chloride, urea, and sucrose.

Results and Discussion

Phase Equilibria. The first simple exercise consists of representing liquid–vapor equilibria by plotting vapor pressure versus temperature. This will aid in observing the general effect of solute on vapor pressure (See Figures 2 and 3).

Inspection of Figure 2 shows that 4 m sodium chloride has a similar effect on vapor pressure to that of 8 m urea. This implies that the type of solute is as important in analyzing vapor pressure lowering as it is in the analysis of the other three colligative properties: boiling point elevation, freezing point depression, and osmotic pressure.

The type and amount of solute are of equal importance in their effect on vapor pressure. This is in agreement with the behavior expected when including the activity of the solvent at different temperatures in the expression for Raoult's vapor pressure:

activity (a) = activity coefficient (γ) \times the mole fraction of solvent (X_{solvent})

and

Raoult's vapor pressure (P) = pure solvent pressure (P°) \times [activity (a) / activity coefficient (γ)]

Because the activity coefficient is dependent on the type of solute used, Raoult's pressure is also dependent on type of solute. The dependency of Raoult's pressure on the type of solute mandates that vapor-pressure lowering is also dependent

on the type of solute. This concept is usually not made as clear in general chemistry textbooks, and sometimes statements on vapor-pressure lowering are misleading students to think that vapor pressure is the only colligative property that is affected only by the amount of solute and not by the type [1–4].

In the following section we will prove further that heat of vaporization is affected by the type of solute and type of intermolecular forces between solvent and solute molecules.

The Clausius–Clapeyron Equation. The Clausius–Clapeyron equation relates the vapor pressure and the heat of vaporization through the following equation.

$$\log P = \frac{-\Delta H_{\text{vap}}}{2.303RT} - \frac{\Delta S}{2.303R}$$

Graphs of $\log P$ versus $1/T$ are constructed for all data sets. The slopes and intercepts of these plots are determined using linear regression (Table 1). ΔH_{vap} and ΔS_{vap} are then calculated from the slope and intercept, respectively.

An inspection of the values in the last column of Table 2 gives an indication of some initial change in heat of vaporization as a certain solute is added. After that initial change the value is not affected significantly, even at higher molalities of the same solute. For example, ΔH_{vap} increases by about 1 kJ, over that in pure water, when one molal sodium is used, but there is no significant change when NaCl is increased from 1 m to 4 m. In the case of urea, there is an increase of 2 kJ for ΔH_{vap} when 4 m solution of urea is used in place of pure water. The change in ΔH_{vap} is almost zero when the molality of urea was increased from 4 to 8. Although the sucrose data shows a larger random error (because of polymerization resulting from the continuous heating), the general trend is still very clear. There is about a 3 kJ increase in ΔH_{vap} for a 0.68 m sucrose solution over that for pure water, but when the molality of sucrose is doubled the change is insignificant. This analysis indicates that vapor-pressure lowering is not only dependent on the type and amount of solute, but that the solute effect is of greater influence in the initial stage of vaporization.

Raoult's Law and the Clausius–Clapeyron Equation. Additional exercises involve analysis of all the data sets applying Raoult's law and calculating the vapor pressure of the solvent, P° . Raoult's law relates P° to the solvent pressure in the presence of a solute, P_{Raoult} as $P^\circ = P_{\text{Raoult}} / X_{\text{solvent}}$. The procedure is to calculate the mole fraction of water in the sodium chloride, urea, and sucrose solutions. Then, use Raoult's Law and the experimentally determined vapor pressure values (P_{Raoult}) in the presence of nonvolatile solutes to determine the vapor pressure (P°) for pure water.

If Raoult's law and the Clausius–Clapeyron equation are combined, the following relationship is obtained, which can be used to calculate boiling temperatures of pure water at different pressures.

$$\log \frac{P_{\text{Raoult}}}{X_{\text{Raoult}}} = \frac{-\Delta H_{\text{vap}}}{2.303RT} - \frac{\Delta S}{2.303R} \quad (1)$$

Values for ΔH_{vap} and ΔS_{vap} of pure water can be obtained from Table 2 and used in eq 1 to calculate the boiling

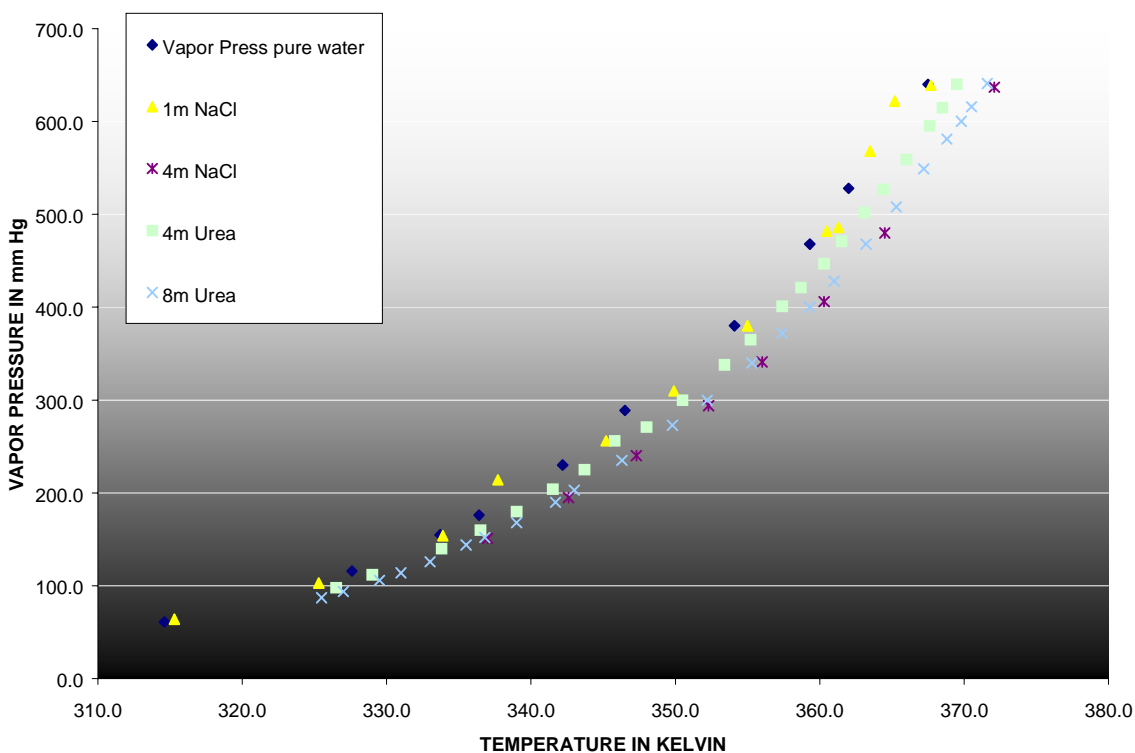


Figure 2. Vapor pressure versus temperature for pure water, 1 m NaCl, 4 m NaCl, 4 m urea, and 8 m urea

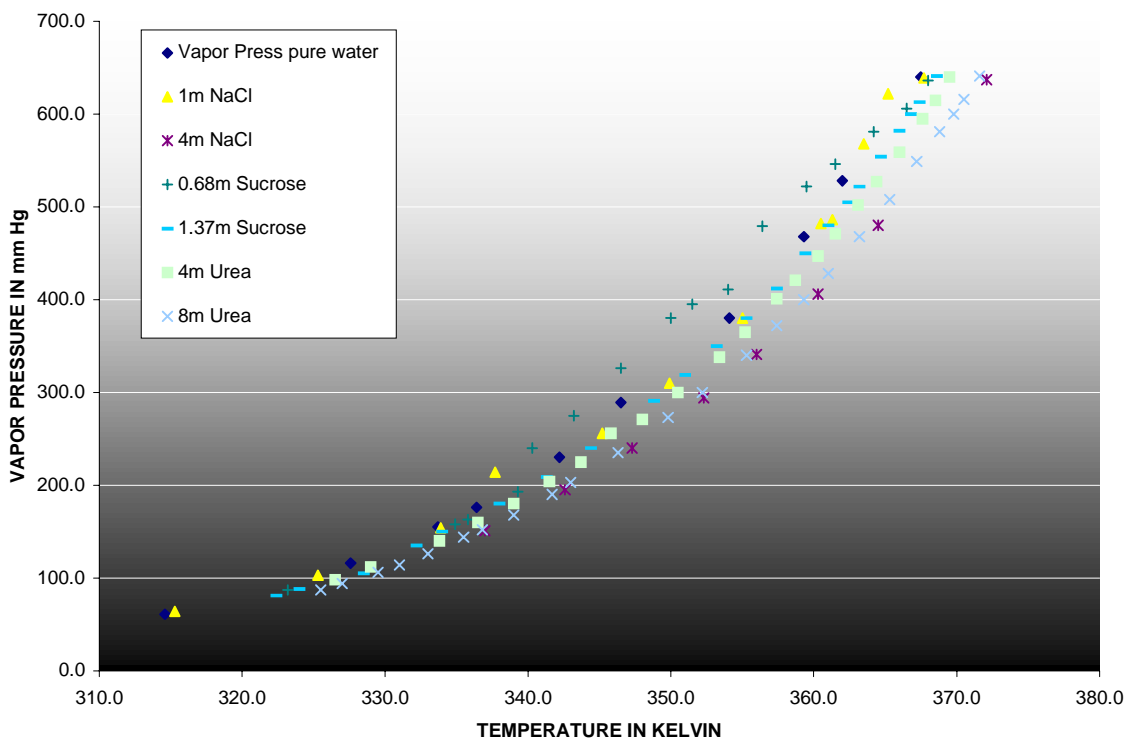


Figure 3. Vapor pressure versus temperature for pure water, 1 m NaCl, 4 m NaCl, 4 m urea, 8 m urea, 0.68 m sucrose, and 1.37 m sucrose.

temperature at the different pressures used. This calculation should be performed for all the solutions. The results obtained represent the boiling temperatures based on Raoult's law. The results from this data analysis are then discussed in terms of deviations from Raoult's law and to observe how the deviation

is related to the concentration of the solute as well as the type of solute used.

Additional experiments can be performed using other ionic compounds, such as LiBr or KBr. Students can predict if the vapor pressure curve is different from the NaCl curve.

Table 1. Slopes from Linear Regression Using the Clausius-Clapeyron Equation

Solution	Slope (negative)	Error Estimates
Pure water	2.173	38
1 m NaCl	2.221	46
4 m NaCl	2.231	7
4 m urea	2.274	11
8 m urea	2.276	6
0.67 m sucrose	2.333	95
1.37 m sucrose	2.313	14

Table 2. Change in Enthalpy and Entropy of Vaporization as Affected by the Presence of Ionic and Molecular Solutes

Solution	ΔH_{vap} (kJ mol ⁻¹)	ΔS_{vap} (J mol ⁻¹ K)	Difference ^a ΔH_{vap} (kJ mol ⁻¹)
Pure Water	41.448	166.5	0.000
1 m NaCl	42.538	169.5	1.090
4 m NaCl	42.718	168.5	1.270
4 m Urea	43.545	171.6	2.097
8 m Urea	43.582	171.1	2.134
0.68 m Sucrose	44.675	176.0	3.227
1.37 m Sucrose	44.299	174.0	2.851

^aValues in this column are obtained by taking the difference between ΔH_{vap} values in the second column and those for pure water as determined in the experiment (41.448 kJ mol⁻¹), which is 1.9% higher than the literature value of 40.79 kJ mol⁻¹. Conclusions

This experiment offers a nice opportunity to bridge the gap between classical thermodynamics and the molecular view. Colligative vapor pressure effects are obtained from the simple idea that a nonvolatile solute occupies potential sites on the solution's surface and thus alters the rate of evaporation. Consequently, only the number of particles supplied by the solute is important because it is assumed that any solute particle can occupy a site and thereby reduce the solvents' escape potential. If this simple model were completely accurate, then we would expect that ΔH_{vap} values for solutions with a common solvent are equal. This implies that the energetics of overcoming the solvent-solvent intermolecular forces, which allows vaporization, is not altered by the solute.

In our experiment we find that there is an initial increase in the magnitude of the slope for the 4 m urea solution over that for pure water, but no significant change is observed when the molality of urea is doubled to 8 m. The same trends are observed for the sodium chloride and sucrose solutions (see Table 1). This must be a result of the energy needed to overcome solute-solvent interaction. This interaction energy is high in the urea solutions and highest in sucrose solutions.

Two processes should be considered in order to explain this trend: the entropy of the solute-solvent system and solute-solvent interactions. Sodium chloride solutions possess a higher degree of order than urea and sucrose solutions. Sucrose solutions are the least ordered. The degree of order must be overcome when water is vaporized from solutions of sodium chloride, thus the process is more entropy driven than when water is vaporized from urea or sucrose solutions. More energy is required to break the solvation sphere in sucrose solutions because of (1) the bulky size of sucrose molecules, which results in entanglement of molecules, (2) the lower

order of the system, which does not result in as significant a change in entropy as occurs in sodium chloride solutions. Sodium chloride solutions possess electrostatic attractions [18] that need to be overcome in the process of vaporization, urea forms hydrogen bonds with water, and in sucrose heat is absorbed through polymerization. Once the electrostatic attraction is overcome in NaCl solutions, the ordering of the system, the solvation sphere, is destroyed, and the process of vaporization becomes entropy driven as seen in the slope changes presented in Table 1.

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- In ionic solutions there is an extra Gibbs free energy that arises from the Debye-Hückel electrostatic interaction between ions. In a nonideal solution this electrostatic energy of interaction is equal to the difference in the Gibbs free energy of the ions in a real solution and the free energy in the ideal solution ($\Delta\mu_{\text{ions}}$)
 $\Delta\mu_{\text{ions}} = RT \ln a_{\text{ions}} - RT \ln C_{\text{ions}}$ or $\Delta\mu_{\text{ions}} = RT \ln \gamma_{\text{ions}}$ where a_{ions} is the activity, C_{ions} is the molar concentration, and γ_{ions} is the activity coefficient at the Kelvin temperature. For example, a 0.5 M aqueous solution of KCl at 25°C exhibits an electrical energy of -2.127 kJ mol⁻¹ extra Gibbs free energy, based on γ_{ions} of 0.95 kJ mol⁻¹. A 1 m sodium chloride solution ($\gamma_{\text{ions}} = 0.66$) at 25°C exhibits an extra Gibbs free energy of -2.060 kJ mol⁻¹, while a 4 m solution ($\gamma_{\text{ions}} = 0.78$) exhibits a value of -1.230 kJ mol⁻¹ [1].