Analysis of Critical Point Phenomena in Binary Liquid Systems

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Introduction

In 1970, Robert Griffiths and John Wheeler published a paper focusing on exploring the various properties of a system with multiple components near the critical point. In order to clarify their theory, they began by dividing all of the variables into two primary categories based on how they exist across a phase boundary. Field variables such as temperature, pressure, and chemical potential are identical across a phase boundary, when the system is at equilibrium. Density variables such as solubility and extent of reaction are different in each phase.

It was then explained that certain divergences of the system as it approached the critical point could be predicted by the equilibrium properties of that system. When the derivative of a density variable with respect to a field variable is calculated, the number of fixed density variables can effect the manner of divergence from the normal trend. If no density variables are held fixed, then there is a "strong" divergence. When a single density is held fixed, a weak divergence can be observed. However, if two or more densities are fixed, then no divergence from the general trend can be observed. An algorithm combining aspects of Brinkley and Jouget matrices was developed by Josh Lang to find the number of fixed densities for a given system and relate them to the degrees of freedom f using a modified form of Gibb's phase rule. If f=2, a strong effect is expected, whereas if f=3 a weak effect is expected. If f > 3, then no effect is expected. It was decided to find a solubility experiment with a strong divergence (f=2) in order to test the theory.
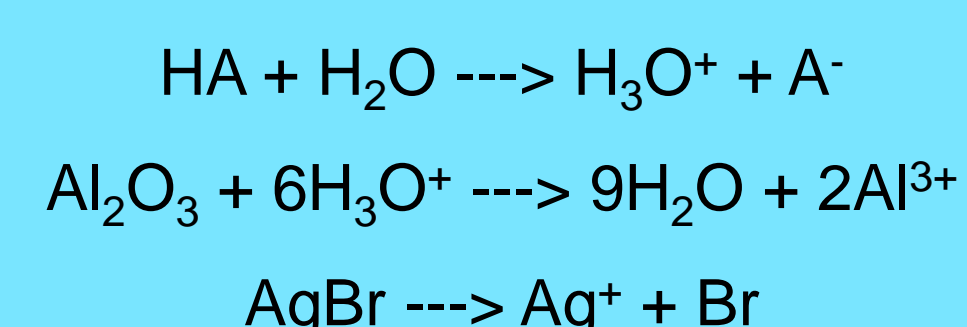
Test: Solubility of Silver Bromide and Aluminum Oxide

When silver bromide and aluminum oxide are introduced into the single phase mixture of isobutyric acid and water, the following reactions take place (A represents the isobutyrate anion):

$$HA + H_2O ---> H_3O^+ + A^-$$

$$Al_2O_3 + 6H_3O^+ ---> 9H_2O + 2Al^{3+}$$

$$AgBr ---> Ag^+ + Br$$

As proven via Brinkley analysis, f=2 for this experimental setup, where the two field variables held constant are temperature and pressure. This means that no densities are fixed, and the Griffiths and Wheeler postulates suggest that a strong critical effect can be observed as the solution nears its critical temperature of approximately 26.2 °C. In this case, the density variable is the solubility of silver and aluminum ions, which will be tested with respect to temperature, a field variable. Hence, it is expected that solubility of these ions trend strongly upward or downward as the temperature of the solution approaches T_c. This was to be done at the critical composition (38.8% mass isobutyric acid) as to approach the critical point from the peak of the coexistence curve.

Setup and Procedure

A solution of 38.8 mass percent isobutyric acid (IBA) and deionized water was made and combined with 0.5 g silver bromide and 1.0 g aluminum oxide. These were placed inside a small stoppered glass reaction vessel, which was held at constant temperature by an insulated aquarium inside a darkroom, owing to the photosensitivity of the silver bromide. The temperature in the aquarium was maintained by means of a thermoregulator linked to a heating element, and a small motorized impellor was employed to ensure even dissipation of the heat introduced. The temperature was monitored by means of a large platinum resistance thermometer, calibrated to equalize to within 0.03 °C. Finally, a stir bar was placed in the reaction vessel, and its respective stir plate was placed under the glass bottom of the elevated aquarium so that the solution could be mixed at will.

Every day at 10:15 A.M. a 10 mL sample of the solution is pipetted from the reaction vessel into a centrifuge tube covered in black electrical tape to prevent light contamination. Five mL of spectroscopic grade nitric acid is then added to the tube to stabilize the sample, which is the sealed and the lid covered with more black tape. By 10:45, the temperature in the tank has been stabilized by the thermoregulator to the next desired point, and the stir plate is turned on high enough to ensure that the entire reaction vessel is being mixed. Throughout the day, the temperature was monitored by the resistance thermometer. At 5:30 P.M. stirring stopped, and the solution was allowed to settle until 10:15 the next morning, upon which time the entire process would be repeated. If necessary, addition IBA/water solution was added to the reaction vessel. The silver and aluminum ion concentrations will be checked with Atomic Absorbance spectroscopy.

Discussion

Use of Silver Bromide and Aluminum Oxide

Since both aluminum oxide and silver bromide are sparingly soluble, but their ions are easily soluble in solution, it was determined that they would be ripe candidates for a solubility-based experiment. Even when taking into consideration the fact that fresh IBA/water was added to the reaction vessel, the amounts of these compounds utilized were in excess of what the solution could dissolve by orders of magnitude. Thus, they never needed replenishing. Furthermore, the time period allotted for settling was of great importance. If the solution had not completely settled, some of the particulate would still be suspended in the solution, and since it is not in ion form, the concentration values of the metals would be artificially inflated. Thus, the use of sparing soluble compounds made it easier to settle out any suspended particulate and attain more accurate data.

Thermometer Calibration

The platinum resistance thermometer had to be calibrated to the actual temperature, since it was observed that the resistance values did not match the calculated temperature. To remedy this, the large thermometer probe was placed in a beaker of water along with two other thermometers of known accuracy. The water was cooled from 30°C to 20°C, and the measured resistance was recorded with every 0.1°C drop. This data was plotted in Excel, and a regression function was calculated. The data was perfectly linear, enabling the function values to be extrapolated to whatever temperature was required for the experiment.

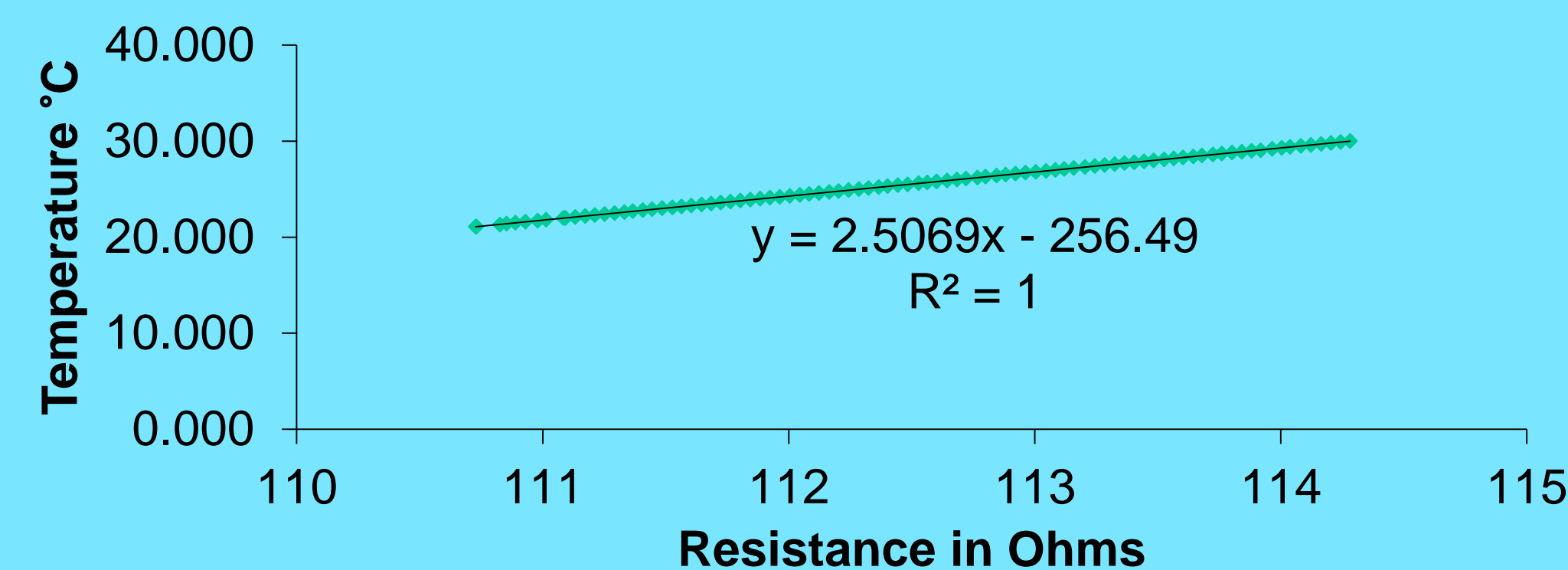**Platinum Resistance Thermometer Calibration**

$y = 2.5069x - 256.49$
$R^2 = 1$

Figure 1. The temperature vs. resistance calibration curve used to determine the temperature at which to take various samples.

Results

Van't Hoff plot for [Ag] vs. T
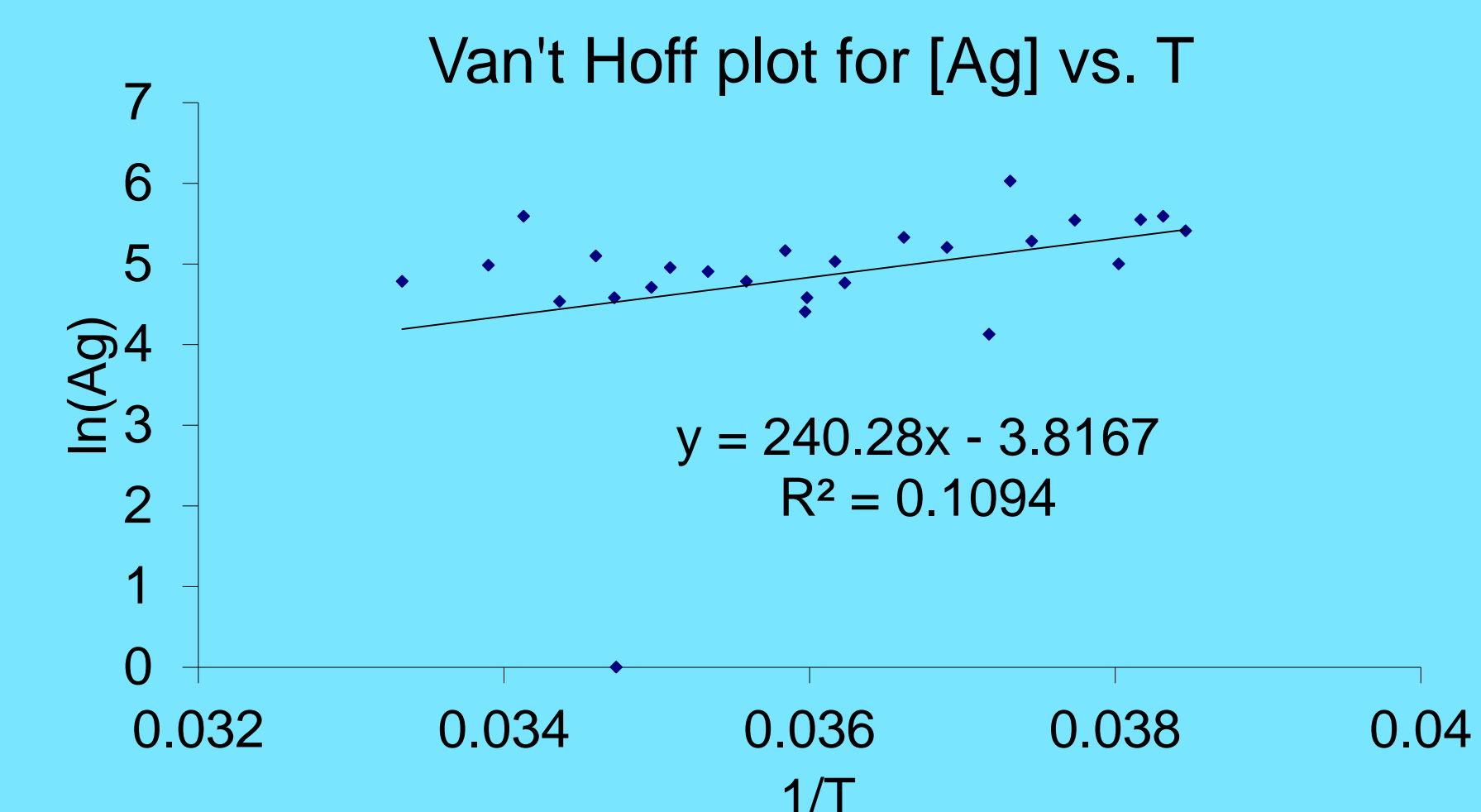
$y = 240.28x - 3.8167$
$R^2 = 0.1094$

Figure 2. Van't Hoff plot of the concentration of silver ions vs. temperature.

As shown above, there is no clear example of an observable critical effect with regards to solubility as the temperature approaches the critical value. If there is one, it is completely obscured by the noise in the data. Also, the concentrations were so close to the detection limits of the AA unit that the usefulness of the data is limited. Thus, at this point it appears that there needs to be more precise analysis of the solubility data, which can be accomplished by ICP or other methods.