A Test of the Principle of Critical Point Universality in Chemistry

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Introduction

When a binary liquid mixture with a critical point of solution serves as the solvent for a heterogeneous chemical reaction, the liquid phase exchanges mass with at least one non-critical phase with which it is in equilibrium. In this case, the liquid phase constitutes an open system. If some set of the intensive variables can be controlled by the experimenter, there are three possibilities

1. If the fixed intensive variables consist of only the temperature and the pressure, then when the temperature, T, approaches the critical temperature, T_c, (∂ξ/∂T) should diverge as |T−T_c|^{-w}, where w is of the order of one.

2. If the fixed intensive variables consist of the temperature, pressure, and no more than one composition variable, then when T → T_c, (∂ξ/∂T) should diverge as |T−T_c|^{-w}, where w is of the order of 0.1.

3. If the fixed intensive variables consist of the temperature, pressure, and two or more composition variables, then (∂ξ/∂T) should be a smooth function of the temperature as T approaches T_c and thus no critical effect is to be expected.

Materials and Methods

Three systems were created and analyzed. Each system was comprised of either a single solute or solute pair immersed in a reactive binary liquid solvent mixture of 38.8 wt.% isobutyric acid in water.

System #1: Barium Chromate + Sodium Sulfate
System #2: Lead(II) Iodide
System #3: Lead Sulfate + Potassium Iodide

For each system the critical mixture was placed in a flat bottom Pyrex test tube which served as the reaction vessel. The test tube was placed in a constant temperature water bath. The temperature of the water bath was slowly lowered until critical opalescence was observed. Small changes were then made to the temperature to find the critical temperature for the mixture. Once the critical temperature was observed, the temperature was slightly increased and the sample was stirred for 24h followed by 24h of settling. A sample was then taken. The succession temperature change, stirring, settling, and sampling was repeated until the sample was far away from the critical temperature.

Key Findings/Results

These three charts represent the three different systems listed from the previous section. The data points represent the natural log of concentration (s) of Barium or Lead vs. the inverse of temperature in Kelvin. System 1 and System 3 have straight trends, meaning they have no critical effects. System 2 has a critical effect, as seen from the non-linear slope approaching the critical temperature.

The concentration was measured by determining the concentration of the dissolved metal ion in solution. The technique used to quantify the metal ion was inductively coupled plasma spectroscopy (ICP).

Impact/Conclusions

In systems 1 & 3, the application of the Gibbs phase rule for reactive mixtures shows that there are four independent variables. Two of these variables are temperature and pressure. The remaining variables must be composition. As predicted by the theory of critical point isomorphism, there should be no critical effect observed in a system with two fixed composition variables.

In system 2, the application of the Gibbs phase rule for reactive mixtures shows that there are three independent variables. Two of these variables are pressure and temperature. The remaining variable must be composition. As predicted by the theory of critical point isomorphism, there should be a critical effect observed in a system with one fixed composition variables, as the data implies.

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References