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A Test of the Principle of Critical Point Universiality in Chemistry

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This is a letter based on the information provided by the students in the Web form. Additional information about Martin Flores can be found in the attached Academic Transcript.
Please make sure that after selecting the appropriate student you will have all of them informed about your decision. Once you have selected your student of choice resubmit the original proposal with the student information.
Thank you very much for your cooperation.

Joseph Taylor, Bernhard Vogler, David Cook

Project Summary:

A critical point is observed whenever two phases merge in the absence of a phase boundary. For example, when the gas phase disappears and becomes a liquid or when a superconductor becomes a normal conductor. The principal of critical point universality is known to govern phase transitions in physical systems as different as magnets, superfluids, and alloys. As the critical point is approached, the correlation between the positions of the atoms begins to exceed the range of the intermolecular forces. When this happens, the heat capacity becomes infinite, and all systems behave the same. This observation is the basis for the "principle of critical point universality." There has never been a strict test to see if this principle, which is ubiquitous in physics, can be extended to chemical reactions. If we find a critical effect in the chemical experiment which we are proposing below, we will have demonstrated the applicability of the principle to chemistry. If we fail to find a critical effect, we will have proved that the principle does not apply everywhere and does not warrant being termed, "universal." Either way the experiment will be a success!

The mixture, isobutyric acid (IBA) + water is a member of a class of 1000 pairs of liquids known to have a critical point of solution [1]. Above its critical temperature at 26.2 ^{o}C, isobutyric acid and water are completely miscible in one another and form a single liquid phase. Below the critical temperature, the mixture separates into two immiscible liquid layers, reminiscent of oil and water. We have shown experimentally that when KI is dissolved in a mixture of IBA + water and allowed to react with solid $PbSO_4$ to form PbI_2, the concentration, s, of dissolved Pb^{2+} is a smooth function of temperature, T, as T approaches the critical temperature, T_c. Specifically, if we plot the data in the form of $\ln s$ vs. $1/T$, we obtain a straight line. Straight line behavior is expected in this case, because the position of equilibrium is specified by *four* independent variables. By contrast if $PbSO_4$ and PbI_2 are allowed to come to equilibrium in IBA + water in the *absence* of KI, the position of equilibrium is specified by *three* independent variables. The principle of critical point universality [2], which deals specifically with this case, predicts that a plot of $\ln s$ vs. $1/T$ should no longer be a straight line, but

should rather form a curve, the slope of which becomes infinite as T approaches T_c. Our student will perform this crucial experiment. The result will determine if the principle of critical point universality can be extended to chemistry. This experiment was begun last summer. We need to finish it this summer.

Student Duties:

In order to maintain and control a constant temperature in the reaction vessel, the RCEU student will employ the 14 dm^3 water bath located in the Chemical Physics Research Laboratory in MSB 224. The temperature will be measured using a platinum resistance thermometer [3]. The solvent mixture of IBA + water will be prepared at the critical composition by weighing the materials on an analytical balance. The liquid mixture, along with the reactants, will be added to the reaction vessel. The reaction will be allowed to proceed to equilibrium under conditions of continuous stirring using a magnetically controlled stirring bar. Periodically, the student will extract a sample from the reaction mixture using a seriological pipet. The sample will be diluted out of the critical region with 2% nitric acid in order to prevent precipitation of Pb^{2+}. Once a number of samples have been collected, they will be analyzed for their lead content, s, using an atomic absorption spectrophotometer. The student will plot the data in the form $\ln s$ vs. $1/T$ to demonstrate the expected divergence in the slope. The results of this experiment will be published in the refereed literature.

Supervision:

The student will work with graduate student Josh Lang. The research group meets daily with Dr. Baird in the MSB 117 conference room for discussion of theory, experimental technique, and methods of data reduction.

References: (Bold face denotes RCEU undergraduate or a high school volunteer).

1. B. Hu and J. K. Baird, *Int. J. Thermophys.* **31**, 717 (2010).
2. **T. J. Giesy**, **A. S. Chou**, R. L. McFeeters, J. K. Baird, and D. A. Barlow, *Phys. Rev. E* **83,** 061201 (2011).
3. C. D. Specker, **J. M. Ellis**, and J. K. Baird, *Int. J. Thermophys.* **28**, 846 (2007).