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A Test of the Principle of Critical Point Universality in Chemistry

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RCEU Proposal for Summer 2017

Project Title: *A Test of the Principle of Critical Point Universality in Chemistry*.

Faculty Sponsor:

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Project Summary:

A critical point is observed whenever the boundary separating two phases of matter disappears and the phases merge. For example, when a liquid phase becomes a gas or when a superconductor becomes a normal conductor. As the critical point is approached in each of these systems, the correlations between the positions of the atoms begin to exceed the range of the intermolecular forces. When this happens, the distinctions between these systems, which depend specifically upon the nature of their intermolecular forces disappear, and the systems behave in analogous ways. For example, the heat capacity of each of these systems becomes infinite as the temperature approaches the critical temperature for the particular system. This similarity of behavior of thermophysical properties forms the basis of principle of critical point universality [1-3] which is known to govern phase transitions occurring in physical systems as different as magnets, superfluids, and alloys.

Our goal is to see if this principle may apply 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 of critical point universality 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 of isobutyric acid (IBA) + water is a member of a class of 1000 pairs of liquids known to have a critical point of solution [1]. Below 26.2 ^oC, isobutyric acid and water are immiscible in one another and form two distinct liquid phases, reminiscent of oil and water. Above 26.2 ^oC, the two phases merge and become a single liquid phase. This behavior qualifies 26.2 ^oC as the critical point for this system. 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 solid PbI_2, the concentration, s, of dissolved Pb^{2+} is a smooth function of temperature, T, as T approaches the critical temperature, T_c [2]. 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 [2]. 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 predicts in this case that a plot of $\ln s$ vs. $1/T$ should no longer be a straight line, but should as T approaches T_c exhibit a slope which diverges toward positive infinity. Our student will perform this crucial experiment. We know from previous experience that experiments of this type can be easily completed in 10 weeks.

Student Prerequisite: CH 123 General Chemistry II or equivalent.

Student Duties:

- Create, calibrate and maintain an isothermal water bath.
- Prepare a critical composition of Isobutyric Acid + Water.
- Prepare a saturated metal oxide solution using the critical solvent.
- Manage the mix/settle cycle for each sampling temperature of the system.
- Extract samples via pipette at each sampling temperature for the system.
- Prepare the samples for analysis by nitric acid dilution.
- Analyze the samples for metal concentration using UV/Vis or AAS.
- Prepare a van't Hoff plot of the data to test for critical point universality.
- Present the findings at the RCEU poster session
- Collaborate on the submission of a manuscript containing the student's results to a peer reviewed journal.

Supervision:

The student's laboratory work will be under the direct supervision of Josh Lang. The work will be performed in the Chemical Physics Research Laboratory in MSB 224. The student's work will be monitored daily through a combination of face to face as well as electronic communication and by a weekly meeting in the MSB 117 conference room for discussion of theory, project status, experimental technique, and methods of data analysis.

References

1. B. Hu and J. K. Baird, *Int. J. Thermophys.* 31, 717 (2010).
2. J. K. Baird, J. D. Baker, B. Hu, J. R. Lang, K. E. Joyce, A. K. Sides, and R. D. Richey *J. Phys. Chem. B* 119, 4041 – 4047 (2015).
3. T. J. Giesy, A. S. Chou, R. L. McFeeters, J. K. Baird, and D. A. Barlow, *Phys. Rev. E* 83, 061201 (2011).
4. C. D. Specker, J. M. Ellis, and J. K. Baird, *Int. J. Thermophys.* 28, 846 (2007).
5. J. D. Savoy, J. K. Baird, and J. R. Lang, *J. Chromatography A*, 1437 58 - 66 (2016)