Phase rule and isomorphism principle analysis of critical phenomena in multicomponent systems

Xingjian Wang

Follow this and additional works at: https://louis.uah.edu/uah-dissertations

Recommended Citation
https://louis.uah.edu/uah-dissertations/248

This Dissertation is brought to you for free and open access by the UAH Electronic Theses and Dissertations at LOUIS. It has been accepted for inclusion in Dissertations by an authorized administrator of LOUIS.
PHASE RULE AND ISOMORPHISM PRINCIPLE ANALYSIS OF CRITICAL PHENOMENA IN MULTICOMPONENT SYSTEMS

by

XINGJIAN WANG

A DISSERTATION

Submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in The Joint Tricampus Materials Science Program of The University of Alabama The University of Alabama at Birmingham The University of Alabama in Huntsville to The School of Graduate Studies of The University of Alabama in Huntsville

HUNTSVILLE, ALABAMA

2022
In presenting this dissertation in partial fulfillment of the requirements for a doctoral degree from The University of Alabama in Huntsville, I agree that the Library of this University shall make it freely available for inspection. I further agree that permission for extensive copying for scholarly purposes may be granted by my advisor or, in his/her absence, by the Chair of the Department or the Dean of the School of Graduate Studies. It is also understood that due recognition shall be given to me and to The University of Alabama in Huntsville in any scholarly use which may be made of any material in this dissertation.

Xingjian Wang 

6/21/2022

(student signature) 

(date)
DISSERTATION APPROVAL FORM

Submitted by Xingjian Wang in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Materials Science and accepted on behalf of the Faculty of the School of Graduate Studies by the dissertation committee.

We, the undersigned members of the Graduate Faculty of The University of Alabama in Huntsville, certify that we have advised and/or supervised the candidate on the work described in this dissertation. We further certify that we have reviewed the dissertation manuscript and approve it in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Materials Science.

6/17/2022 Committee Chair
(Date)

6/20/2022 Dr. Guangsheng Zhang

6/20/2022 Dr. Lingze Duan

6/20/2022 Dr. Gregory Thompson

6/14/2022 Dr. Robert Frederick

6/27/2022 Program Director

College Dean

Graduate Dean
ABSTRACT
The School of Graduate Studies
The University of Alabama in Huntsville

Degree Doctor of Philosophy
Program Materials Science

Name of Candidate Xingjian Wang

Title Phase Rule and Isomorphism Principle Analysis of Critical Phenomena in Multicomponent Systems

This dissertation investigates critical phenomena in liquid mixtures near the liquid–liquid critical solution temperature, concentrating on critical effects in solubility and turbidity. According to the Principle of Critical Point Isomorphism, which is thought to govern all critical phenomena, a critical effect is expected in the temperature dependence of the mole fraction of a solute in the case where fewer than two other mole fractions are held fixed. The phase rule is used to enumerate the fixed variables and identify such cases.

The solubility experiments, which are the subject of this dissertation, involve measurements on binary liquid solvents supporting up to ten chemical components participating in as many as four simultaneous chemical reactions. In each case where there is an excess of a solid present, it is found by plotting the concentration of the corresponding solute in van’t Hoff form with the logarithm of the solubility vs. the reciprocal of the temperature, that the data lie on a straight line at temperatures away from critical. The critical effect manifests itself in a divergence of the slope of the van’t Hoff plot near the critical temperature. The divergence in the slope is in the negative sense when dissolution is endothermic and in the positive sense when the dissolution is exothermic. Application of
the phase rule to each case indicates that the number of fixed mole fractions is less than two, thus confirming the universality principle.

The turbidities of seven binary liquid mixtures were measured by laser light scattering. In each case, the path of approach to the critical point was along the critical isopleth in the homogeneous phase. Critical opalescence was observed in every system. A phase rule calculation indicates that in each system, one mole fraction was fixed. This calculation, plus the observation of opalescence, confirms the universality principle. When a completely soluble solute is added to the binary mixture, the opalescence disappears completely. The phase rule indicates that two mole fractions are fixed in this case. The observed quenching of critical opalescence by addition of solute is thus in complete agreement with the universality principle.
ACKNOWLEDGMENTS

Firstly, I would like to thank my advisor, Professor James K. Baird, for his support and advice throughout my four years of study in my Ph.D. program. I would not have completed the required research work and dissertation without his guidance and encouragement.

I deeply appreciate and acknowledge the other committee members, Dr. Robert Frederick, Dr. Emanuel Waddell, Dr. Linze Duan, Dr. Gregory B. Thompson, and Dr. Guangsheng Zhang, for their helpful suggestions and review of this dissertation.

I want to thank all the members of our research group for their help and support during my research work. In particular, I wish to thank Dr. Joshua Lang for his help setting up the experimental, and Pauline Noris for providing the ICP analysis of my samples at Western Kentucky University.

I would like to thank Dr. Bernhard Vogler, Dr. Sharifa Love-Rutledge, and Dr. Jeffery Weimer for providing my research's chemical materials and research facility. Part of this research was done in Dr. Junpeng Guo’s optics lab. Many thanks go to him and Dr. Jinnan Chen for helping me set up the optics instruments.

I would like to thank the chemistry department staff, Jeffery Champoux, who helped me a lot in academic affairs.

I also want to thank my parents, Bo Wang and Fang Bao, and my wife, Maiji Wu, and daughter, Youyou Frances Wang. Their love has always supported me to conquer any difficulties.
Table of Contents

Table of Contents ....................................................................................................................... vii
List of Figures ............................................................................................................................... ix
List of Tables ................................................................................................................................. xi

CHAPTER 1 INTRODUCTION ........................................................................................................ 1
  1.1 Introduction to Critical Phenomena ......................................................................................... 1
  1.2 A Brief Review of Research on Critical Point Phenomena ....................................................... 4
  1.3 Objectives of Study ................................................................................................................ ....6
  1.4 Organization of the Dissertation............................................................................................... 11

CHAPTER 2 THEORY OF PHASE TRANSITIONS AND CRITICAL PHENOMENA ...13
  2.1. The Universality of Critical Point Phenomena .................................................................. 13
  2.2. The Scaling Property of Critical Point Phenomena ............................................................ 32
    2.2.1. Isochoric Heat Capacity $C_V \sim t^{-\alpha}$ ........................................................................ 33
    2.2.2. Coexistence Curve $x \sim t^{\beta}$ ...................................................................................... 36
    2.2.3. Response Function $\kappa \sim t^{-\gamma}$ .............................................................................. 37
    2.2.4. Critical Isotherm $\mu \sim x^\delta$ ....................................................................................... 38
  2.3. The Classification of the Critical Behavior ......................................................................... 40
  2.4. A Generalized Phase Rule Analysis of Critical Phenomena ............................................... 45

CHAPTER 3 THE REGULAR SOLUTION MODEL FOR MULTICOMPONENT SYSTEMS ........................................................................................................ 49
  3.1 Critical Points in Ternary Systems ......................................................................................... 49
  3.2 The Supercritical Solubility in Multicomponent Systems ..................................................... 55
  3.3 The Critical Opalescence in Multicomponent Systems .......................................................... 61

CHAPTER 4 THE DISSOLUTION IN MULTICOMPONENT SYSTEMS AT THE CRITICAL POINT ........................................................................................................ 70
  4.1 Experimental Materials .......................................................................................................... 70
  4.2 Experimental Methods .......................................................................................................... 73
  4.3 The Dissolution of Phenolphthalein in Nitrobenzene + Dodecane ........................................ 77
  4.4 The Dissolution of Barium Chromate in IBA + Water .......................................................... 80
  4.5 The Dissolution of Gallium (III) Oxide in IBA + Water .......................................................... 83
4.6 The Dissolution of Zinc (-)-Tartrate in IBA + Water ...................................................... 86
4.7 The Dissolution of Glutamic (-)-Acid in DGME + Water .............................................. 89
4.8 The Dissolution of Lead Iodide and Sodium Sulfate in IBA and Water Mixture .......... 93
4.9 The Dissolution of Lead Iodide and Lead Sulfate in IBA and Water Mixture .......... 96
4.10 The Dissolution of Barium Sulfate and Calcium Sulfate in IBA and Water Mixture.... 100
4.11 The Dissolution of Zinc (+)-Tartrate and Zinc (-)-Tartrate in IBA + Water Mixture .... 104
4.12 Discussion .................................................................................................................... 107

CHAPTER 5 THE SUPPRESSION OF CRITICAL OPALESCENCE IN MULTICOMPONENT SYSTEMS ................................................................................................................. 111

5.1 Experimental Materials ................................................................................................... 111
5.2 Experimental Methods .................................................................................................... 113
5.3 The Suppression of Critical Opalescence in Binary Mixtures ..................................... 115
  5.3.1 The Effect of Refractive Indices ................................................................................ 115
  5.3.2 The Effect of an Inert Solid ...................................................................................... 118
  5.3.3 The Effect of a Reactive Solid ................................................................................ 120
5.4 The Critical Opalescence in Ternary Liquid Mixtures .................................................... 129
5.5 Discussion ..................................................................................................................... 132

CHAPTER 6 SUMMARY .......................................................................................................... 134

REFERENCES ....................................................................................................................... 137
List of Figures

Figure 1. Ferromagnetic-Paramagnetic Phase Transition ................................................................. 2
Figure 2. Phase Diagram of isobutyric acid and water mixture ......................................................... 6
Figure 3. An example of densities, \( \rho \), and fields, \( h \), in coexistence phases ................................. 7
Figure 4. Graphical solution of the transcendental equation .............................................................. 18
Figure 5. The plot of free energy vs. magnetization ........................................................................... 19
Figure 6. Isotherms for van der Waals gas. The dashed curve is the coexistence curve ................. 22
Figure 7. Graphical solution of the self-constraint equation of molar fraction of a binary mixture ................................................................. 28
Figure 8. Schematic behavior of \( \partial^2 \Delta G_{\text{mix}} / \partial x_1^2 \) for three different temperatures .............. 29
Figure 9. Liquid-vapor coexistence curve and critical point for a pure fluid .................................... 40
Figure 10. Schematic illustration of critical end points ....................................................................... 50
Figure 11. Phase diagram of DGME + water mixture ......................................................................... 72
Figure 12. Schematic diagram of water bath apparatus ..................................................................... 74
Figure 13. The experimental procedure for the critical point determination ...................................... 75
Figure 14. Van’t Hoff plot of the temperature dependence of the solubility of phenolphthalein in nitrobenzene + dodecane mixture ..................................................................................... 79
Figure 15. Van’t Hoff plot of the temperature dependence of the solubility of barium in IBA + water .................................................................................................................. 82
Figure 16. Van’t Hoff plot of the temperature dependence of the solubility of gallium in IBA + water .................................................................................................................. 85
Figure 17. Van’t Hoff plot of the temperature dependence of the solubility of zinc in
IBA + water ............................................................................................................................................. 88

Figure 18. Chemical structures of glutamic (-)-acid................................................................................. 89

Figure 19. Van’t Hoff plot of the temperature dependence of the solubility of

glutamic (-)-acid in DGME + water ........................................................................................................ 92

Figure 20. Van’t Hoff plot of the temperature dependence of the solubility of lead sulfate in

IBA + water ............................................................................................................................................. 96

Figure 21. Van’t Hoff plot of the temperature dependence of the solubility of lead in

IBA + water ............................................................................................................................................. 99

Figure 22. Van’t Hoff plot of the temperature dependence of the solubility of barium in

IBA + water mixture .................................................................................................................................. 102

Figure 23. Van’t Hoff plot of the temperature dependence of the solubility of calcium in

IBA + water mixture .................................................................................................................................. 103

Figure 24. Chemical Structures of Zinc (-)-Tartrate (left) and Zinc (+)-Tartrate (right)........... 104

Figure 25. Van’t Hoff plot of the temperature dependence of the solubility of zinc in the

IBA + water ............................................................................................................................................. 106

Figure 26. Comparison of strong critical effect and weak critical effect.......................... 109

Figure 27. Schematic diagram of apparatus......................................................................................... 113

Figure 28. Temperature dependence of turbidity of binary mixtures of nitromethane +

ethylene glycol and 1-nonanol + ethylene glycol ............................................................................. 117

Figure 29. Temperature dependence of turbidity from nitrobenzene + dodecane w/wo

cholesterol .............................................................................................................................................. 119

Figure 30. Temperature dependence of turbidity from methanol + hexene w/wo cholesterol... 120

Figure 31. Temperature dependence of turbidity from isobutyric acid + water w/wo NaCl..... 122
Figure 32. The phase diagram of 2,6-lutidine + water................................................................. 125
Figure 33. Temperature dependence of turbidity from 2,6-lutidine + water w/wo NaCl........ 127
Figure 34. Temperature dependence of turbidity from ethylene glycol + nitromethane w/wo 1-dodecanol.......................................................................................................................... 130
Figure 35. Temperature dependence of turbidity from 1-nonanol + nitromethane w/wo ethylene glycol......................................................................................................................... 131
List of Tables

Table 1. Power laws and critical exponents for pure fluids and magnets.................................2
Table 2. Summary of the dissolution of metal oxides in IBA + water .....................................8
Table 3. Values of critical point exponents

<table>
<thead>
<tr>
<th>Critical exponent</th>
<th>31</th>
</tr>
</thead>
</table>
Table 4. The reaction mixtures, sample preparations, and measurements for solubility experiments........................................................................................................71
Table 5. The summary of the critical phenomena in solids dissolving in liquid binary mixtures .............................................................................................................................110
Table 6. Summary of selected binary mixtures and solutes................................................................112
CHAPTER 1 INTRODUCTION

1.1 Introduction to Critical Phenomena

The transition between a stable phase to another usually causes an abrupt, discontinuous change in the properties of the system, such as the enormous change in density when water becomes steam. At the critical point, the discontinuous change turns into a continuous change. Singularities may be observed for some properties in a phase transition that occurs at the critical point. The divergence behavior of these properties, such as the specific heat capacity in a pure fluid and the conductivity in a superconductor at the critical point, is known as critical phenomena.

The critical phenomena represent transitions from order to disorder. The order parameter is defined in such a way as to distinguish one phase from another. In the vicinity of the critical point, where the phase boundaries start to vanish, there are fluctuations in the order parameter which grow in spatial extent in a self-similar pattern. For example, in a ferromagnet, there is a net magnetization at temperatures below the Curie temperature (critical temperature for magnetization). As the Curie temperature is approached, the net magnetization diminishes continuously, disappearing altogether at the critical temperature. The phase above the critical temperature is said to be paramagnetic, as shown in Fig.1.
One of the most important properties of critical phenomena is isomorphism. For systems in the same universality class, the principle of critical point isomorphism (also called the principle of critical point universality) suggests the identity of critical behaviors among systems, despite their different physical or chemical natures. [1] The concept of universality class refers to the physical dimensions of the system. Pure fluids, liquid mixtures, and ferromagnets are three-dimensional and belong to the same universality class.

Table 1. Power laws and critical exponents for pure fluids and magnets

<table>
<thead>
<tr>
<th></th>
<th>Pure fluid</th>
<th>Magnet</th>
<th>Power laws</th>
<th>Critical exponent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heat capacity</td>
<td>$C_V$</td>
<td>$C_H$</td>
<td>$\sim</td>
<td>T - T_C</td>
</tr>
<tr>
<td>Coexistence curve</td>
<td>$\Delta V$</td>
<td>$M$</td>
<td>$\sim</td>
<td>T - T_C</td>
</tr>
<tr>
<td>Response function</td>
<td>$\kappa_T$</td>
<td>$\chi_T$</td>
<td>$\sim</td>
<td>T - T_C</td>
</tr>
<tr>
<td>Critical isotherm</td>
<td>$P - P_C$</td>
<td>$H$</td>
<td>$\sim</td>
<td>T - T_C</td>
</tr>
</tbody>
</table>

In the critical region, $T \to T_C$, the divergence of thermodynamic properties is described by the power law, $\sim |T - T_C|^{-x}$, which $x$ is the critical exponent. Table 1 shows the example of these exponents for a pure fluid and a magnet. Because of the principle of critical point isomorphism, the critical exponents of systems in the same universality class have the same value. For example, in the critical region, the magnetic susceptibility, $\chi_T$, is governed by the same critical exponent $\gamma$, $\chi_T \sim |T - T_C|^{-\gamma}$ for all magnets.
The relationship between the critical exponents is provided by the scaling laws [2]

\[ \alpha + \beta(\delta + 1) = 2 \]
\[ \gamma = \beta(\delta - 1) \]
\[ \alpha + 2\beta + \gamma = 2 \]  

(1.1)

The scaling law stems from the hypothesis that the Gibbs free energy, \( G \), is a generalized homogeneous function in the critical region. The scaling law is supported by numerous experiments which include the high-precision measurements of the critical exponents performed in the space shuttle to avoid the limitations of earth gravity. [3] According to the scaling laws, it’s sufficient to determine the values of all critical exponents by knowing any two of them.

The singularity that occurs at the critical point is not always guaranteed. Based upon inductive reasoning, Griffiths and Wheeler associated the existence of critical phenomena with the numbers of certain fixed thermodynamic variables. In specifying the derivatives that are affected by a critical point, Griffiths and Wheeler divide the intensive thermodynamic variables into two categories: (1) the field variables, \( h \), which have the same value in all coexisting phases. Examples include the temperature, the pressure, and the chemical potential. (2) The density variable, \( \rho \), which has a distinct value in each coexisting phase. Examples include the mass density and the mole fraction. The Griffiths-Wheeler rule predicts that a thermodynamic derivative in the form of \((\partial \rho / \partial h)_{\rho_k}\) will diverge “strongly” in a system as the critical point is approached along a path where no density variable, \( \rho_k \), is held fixed. If there is one fixed density variable, the derivative will diverge “weakly” at the critical point. In the end, the divergence is absent once the number of fixed density variables exceeds one.
1.2 A Brief Review of Research on Critical Point Phenomena

Since the supercritical fluid was first observed and studied by C. Cagniard de la Tour in 1822 [4,5], the critical phenomenon has been a very active area of research for two hundred years. In 1869, the term “critical point” was created by T. Andrews who studied the supercritical phase of carbon dioxide. [6] Based on the model in which the interaction between molecules in a fluid was modeled as a hard-core repulsion coupled with a long-range attraction, van der Waals explained Andrews’s experiment by equations of state of the pure fluid in his doctoral thesis in 1873. During the research on the phase transition from ferromagnets to paramagnets, P. Curie discovered the similarity of critical behavior between the ferromagnets and pure fluids. Therefore, he introduced the important concept of “universality” in his mean-field theory to describe the phase transition of ferromagnetic materials. [7] The mean-field theory was generalized by L. D. Landau to give a comprehensive theoretical description of critical phenomena in all universality classes in 1936. [8] Landau and V. Ginzburg then revised the theory to describe superconductivity [9], probably the most famous critical phenomenon, which was discovered by K. Onnes in 1911.

Although Landau’s theory perfectly explains the phenomenon of universality, it fails to give values for the critical point exponents which have been determined experimentally. In 1925, a quantitative statistical mechanical model of the critical phenomena, the Ising-Lenz model, was proposed by W. Lenz and E. Ising. They evaluated the canonical partition function for the case of a linear array of spins. [10,11] However, the two-dimensional Ising model was not solved until 1944 by L. Onsager [12]. Subsequently, C. N. Yang [13] provided a more accessible derivation of Onsager’s theory. Although an analytical solution to the three-dimensional Ising model has not been found and is probably believed impossible, a combined numerical/analytical approach, called...
renormalized group theory, was developed by K. Wilson in 1971. [12] Wilson was able to give a precise prediction of the critical exponents in three dimensions which agreed with the experiment.

The study of critical phenomena in chemistry was started by Krichevskii in reaction equilibrium in 1969 [13], the field has been expanded to include, for example, complex formation, unimolecular decomposition, photoreduction, dehydrogenation, and pyrolysis in the past forty years. [14] By 1970, enough data has accumulated that a pattern was identified by Griffiths and Wheeler in which the critical phenomena depend on the numbers of certain fixed variables. [15] The application of the Griffiths-Wheeler requires the knowledge of fixed independent intensive thermodynamic variables which is difficult in the case of heterogeneous chemical equilibria involving several substances where dozens of variables are involved. To leverage the full potential of Griffiths-Wheeler theory for predicting the critical effects in multicomponent systems, Baird et al. exploited [16–30] a generalized Gibbs phase rule [31] to determine the number of fixed thermodynamic variables.

In this dissertation, the phase rule and critical isomorphism principal analysis are applied to the dissolution in complicated multicomponent systems. The result of those experiments also has inspired us to develop a method to suppress the critical opalescence, a light scattering phenomenon occurring at the critical point, of binary mixtures.
1.3 Objectives of Study

The binary mixture system, which belongs to the three-dimension Ising model universality class, has been chosen for our research on the critical phenomena because of its convenient critical temperature and a larger critical region than that of most other systems. [1] For a binary liquid mixture whose phase diagram exhibits a miscibility gap ending in a critical point of the solution, the two liquids are only partially miscible on the concave side to the CXC, whereas they are completely miscible on the convex side, as shown in Figure 2. The extremum of the coexistence curve is called the critical point of the solution. If the extremum is a maximum, as shown in Fig. 2, the critical temperature is an upper critical solution temperature (UCST). If the extremum is a minimum, the critical temperature is a lower critical solution temperature (LCST). The critical point of binary mixtures can easily be determined visually by observing the onset of critical opalescence.

![Figure 2. Phase Diagram of isobutyric acid and water mixture](image)
The application of Griffiths-Wheeler rules in the multicomponent system has been limited by the difficulty in the determination of the number of independent thermodynamic variables required to specify equilibrium in the systems, especially when chemical reactions are involved. The generalized form of the Gibbs phase rule, however, provides a method for determining the total number, \( F \), of intensive thermodynamic variables needed to describe any chemical equilibrium. [31] A phase rule analysis serves as an unambiguous method for counting the number of fixed densities in an experiment.

Figure 3. An example of densities, \( \rho \), and fields, \( h \), in coexistence phases

The Griffiths-Wheeler rule suggests that the degree of the critical effect depends on the number of fixed densities: (a) If there is no fixed density at the critical point, we expect a strong critical effect. (b) If only one density is fixed, a weak critical effect is expected. (c) Otherwise, no critical effect is to be expected. The critical effect is only expected if the number of fixed densities is less than two. Because the temperature and pressure are fixed in the typical heterogeneous
equilibrium, if the system has \( F \) independent variables, the rest of them, \( F - 2 \), variables are necessarily densities. Thus, we expect a critical effect in the cases of \( F \leq 3 \), but when \( F > 3 \), no critical effect is to be expected. Table 2 summarizes previous experiments with metal oxides dissolving in IBA + water from our group. The critical effect was observed in each of these \( F = 3 \) cases and no critical effect was observed in the experiment in which the phase rule analysis gives \( F = 4 \).

Table 2. Summary of the dissolution of metal oxides in IBA + water

<table>
<thead>
<tr>
<th>Solute</th>
<th>( F )</th>
<th>Critical effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper(II) Oxide</td>
<td>3</td>
<td>Yes</td>
</tr>
<tr>
<td>Tin(II) Oxide</td>
<td>3</td>
<td>Yes</td>
</tr>
<tr>
<td>Cobalt(II) Oxide</td>
<td>3</td>
<td>Yes</td>
</tr>
<tr>
<td>Nickel(II) Oxide</td>
<td>3</td>
<td>Yes</td>
</tr>
<tr>
<td>Aluminum Oxide</td>
<td>3</td>
<td>Yes</td>
</tr>
<tr>
<td>Iron(III) Oxide</td>
<td>3</td>
<td>Yes</td>
</tr>
<tr>
<td>Cobalt (II, III) Oxide</td>
<td>3</td>
<td>Yes</td>
</tr>
<tr>
<td>Indium (III) Oxide</td>
<td>3</td>
<td>Yes</td>
</tr>
<tr>
<td>Cerium (IV) Oxide</td>
<td>3</td>
<td>Yes</td>
</tr>
<tr>
<td>Manganese Dioxide</td>
<td>3</td>
<td>Yes</td>
</tr>
<tr>
<td>Barium Peroxide</td>
<td>3</td>
<td>Yes</td>
</tr>
<tr>
<td>Manganese Dioxide and Aluminum Oxide</td>
<td>3</td>
<td>Yes</td>
</tr>
<tr>
<td>Copper (I) Oxide and Aluminum Oxide</td>
<td>3</td>
<td>Yes</td>
</tr>
<tr>
<td>Lead (II) Sulfate</td>
<td>3</td>
<td>Yes</td>
</tr>
<tr>
<td>Barium Sulfate</td>
<td>3</td>
<td>Yes</td>
</tr>
<tr>
<td>Lead Iodide and Lead Sulfate</td>
<td>3</td>
<td>Yes</td>
</tr>
<tr>
<td>Lead (II) Sulfate and Potassium Iodide</td>
<td>4</td>
<td>No</td>
</tr>
<tr>
<td>Aluminum Phosphate</td>
<td>3</td>
<td>Yes</td>
</tr>
</tbody>
</table>

1.3.1. **Critical effect on solubility**

When the solute is added to a binary liquid mixture, the temperature dependence of the solubility, \( s \), outside the critical region can be described by the van’t Hoef equation
\[
\ln s = \ln s_x - \frac{\Delta H}{R} \left( \frac{1}{T} - \frac{1}{T_x} \right)
\]  

(1.2)

where \( s \) is the solubility at \( T \), \( s_x \) is the solubility at \( T = T_x \), \( \Delta H \) is the enthalpy of solution, and \( R \) is the gas constant.

In the critical region, the slope of a plot of the van’t Hoff equation is a function of the derivative of the natural logarithm of solubility with respect to the difference of Gibbs free energy,

\[
\left[ \frac{\partial \ln s}{\partial (1/T)} \right]_{T \to T_c} = -T \Delta H \left( \frac{\partial \ln s}{\partial \Delta G} \right)
\]  

(1.3)

Because \( \ln s \) is a density variable and \( \Delta G \) is a field variable, the \( \left( \frac{\partial \ln s}{\partial \Delta G} \right) \) is expected to diverge if there is no more than one fixed density variable. As a result, we are able to predict the behavior of solubility in the critical region solely by counting the number of fixed density variables.

In this dissertation, the phase rule and isomorphism principle analysis is used for the first time to investigate the critical effect on solubilities at the heterogeneous equilibrium not involving a chemical reaction. In the case of previous metal oxide + IBA + water experiments, the metal behaved as a metal, and the acid reacted with the oxygen. An experiment is designed to demonstrate a critical effect involving a metal (chromium) acting as a non-metal. The resulting chromate to dichromate transformation constitutes the first demonstration of a critical effect in a condensation reaction. Another experiment is designed to interchange the acid/base role between the solvent and solute by using a solvent with a basic component to dissolve an acidic solute. Moreover, by eliminating the potassium ion in the dissolution of lead sulfate and potassium iodide in IBA + water, which \( F = 4 \) as shown in Table 2, a stringent test of the phase rule is performed in the case of \( F = 3 \). The critical effect on solubility which has been observed is considered a
“weak” effect because the Griffiths-Wheeler rule suggests that the weak divergence occurs when there is but one density variable fixed at the critical point. By contrast, if there is no density variable fixed at the critical point the solubility of solute becomes strongly divergent at the critical point. We have designed a solubility experiment to observe the strong critical effect on solubility. This serves as another stringent test of the phase/Griffiths Wheeler analysis.

1.3.2. Critical effect on turbidity

The critical point of pure fluids and binary liquid mixtures is usually determined visually by observing the critical opalescence, which is a light scattering phenomenon that only occurs in the critical region. The fact that the critical opalescence was observed for numerous systems, such as carbon disulfide, ether, carbon dichloride, sulfur dioxide, pentane, etc., stimulated scientists to study the isomorphism of critical phenomena in the late nineteenth century.

The critical opalescence is a result of Rayleigh scattering and can be interpreted by the Einstein-Smoluchowski theory. [32,33] These authors contributed the idea that, as the system approaches a critical point, there are fluctuations in relative permittivity (square of the reflective index). The fluctuations have their origin in fluctuations in the concentrations of the chemical components making up the material. The concentration fluctuations can increase in size until they are of the same order of magnitude as the wavelength of the incident light. Hence, although there is no particulate in the system, the concentration fluctuations play the role of scattering particles the same way as the air molecules scattering the visible light which causes the blue sky.
The degree of critical opalescence can be quantified by the measurement of turbidity, $\tau^*$, which is defined as

$$I(x) = I(0) \exp(-\tau^* x)$$

where $I(0)$ is the intensity of the incident light, and $I(x)$ is the intensity of the light transmitted through the thickness, $x$, of the sample.

We have identified the specific thermodynamic derivative, which causes the critical opalescence, by applying the regular solution model. The divergence behavior of the thermodynamic derivative is predicted by the phase rule and universality principal method. The predictions are verified experimentally in several systems with distinctly different physical and chemical properties.

1.4 Organization of the Dissertation

Although the predictive power of the principle of critical point isomorphism, when combined with the phase rule, has found support in the case of several solubility experiments involving solids dissolved in binary liquid mixtures, [16-30] it should be stressed that the universality concept, as presented by Griffiths and Wheeler, is based upon inductive reasoning as opposed to deductive reasoning. Chapter 2 reviews various theoretical models which led Griffiths and Wheeler to enunciate this concept. In Chapter 3, the regular solution model was used to explain
the critical phenomena in multicomponent systems. Chapters 4 and 5 of this dissertation describe a diverse set of new experimental results involving critical points in multicomponent mixtures, which provide convincing empirical evidence in support of the validity of the universality principle. The conclusions and future works appear in Chapter 6.
2.1. The Universality of Critical Point Phenomena

The generalized model of phase transitions in classical theory was given by Landau [8] and Ginzburg [9]. The Landau-Ginzburg theory stems from a mean-field assumption that equates the order parameter to its average, thus ignoring fluctuations. Based on its unified description of phase transitions, the Landau-Ginzburg theory qualitatively interprets the universality of the critical point phenomena among different systems.

In Landau’s description of the phase transition, the order parameter, \( \psi \), describes the orderliness of the system. For an organized system, \( \psi \neq 0 \), but as the system reaches its critical point, the system is entirely disordered, and \( \psi = 0 \). The free energy, \( f \), of a system near the critical point can be expressed in a power series in the order parameter,

\[
f(\psi) = f_0(T) + a_0(T)\psi^2 + \frac{1}{2} b_0(T)\psi^4 + \cdots \tag{2.1}
\]
where the coefficients \( f_0, a_0 \) and \( b_0 \) are functions of temperature \( T \), and the higher order terms are ignored since \( \psi \) is small. The Landau-Ginzburg theory can be applied to any material, including ferromagnetic materials.

2.1.1. Ferromagnets

In this section, we show that the Lenz-Ising model produces the same free energy as the phenomenological Landau-Ginzburg model. In the Lenz-Ising model, only the interactions between the nearest neighbor sites are considered. The Hamiltonian, \( \mathcal{H} \), for the Lenz-Ising model can be written as

\[
\mathcal{H} = -\sum_{\langle i,j \rangle} J \sigma_i \sigma_j - \mu H \sum_i \sigma_i
\]  

(2.2)

where \( J \) is the interaction constant between the nearest neighbor sites, \( \sigma_i \) is the spin of site \( i \) which equals \( \pm 1 \), \( \mu \) is the magnetic moment, \( H \) is the external field, and \( N \) is the total number of sites in the system.

The fluctuations in the mean value of \( \sigma_i \) is defined as

\[
\delta \sigma_i = \sigma_i - \langle \sigma_i \rangle
\]

(2.3)

where \( \langle \sigma_i \rangle \) is the average value of \( \sigma_i \). Substituting Eq. (2.3) into Eq. (2.2), we have

\[
\mathcal{H} = -\sum_{\langle i,j \rangle} J (\langle \sigma_i \rangle + \delta \sigma_i) (\langle \sigma_j \rangle + \delta \sigma_j) - \mu H \sum_i \sigma_i
\]

\[
\Rightarrow \mathcal{H} = -\sum_{\langle i,j \rangle} J (\delta \sigma_i \delta \sigma_j + \langle \sigma_i \rangle \delta \sigma_j + \langle \sigma_i \rangle \delta \sigma_j - \langle \sigma_i \rangle \langle \sigma_j \rangle) - \mu H \sum_i \sigma_i
\]

(2.4)
In the mean-field approximation, the fluctuation is assumed to be small, and the high order of fluctuation can be neglected, so
\[ \delta \sigma_i \delta \sigma_j = 0 \] (2.5)

Because the system has translational symmetry in both the ferromagnet and antiferromagnet states, the value of \( \langle \sigma_i \rangle \) is independent of the value of \( i \). Hence, we define the magnetization, \( M \), as
\[ M = \frac{1}{N} \sum_{i}^{N} \langle \sigma_i \rangle \] (2.6)
which is the order parameter in magnetism.

In this theory, the orderliness of the system increases as the temperature decreases, and its symmetry gets broken below the critical temperature. In the antiferromagnet state of the material, above the critical temperature, the system is entirely disordered because the spins are randomly arranged, as shown in Fig. 1, the average of spins equals zero, \( \langle \sigma_i \rangle = M = 0 \), which suggests spatial symmetry. In the ferromagnet state of the material, below the critical temperature, the magnetization, \( M \), represents the orderliness of the system. Since the value of \( M \) can be either positive or negative, the spatial symmetry is broken because the magnetization points in a certain direction. The critical temperature in ferromagnetism is also termed as the Curie temperature because it was discovered by P. Curie in 1891. [7]

Based on the mean-field theory, the Hamilton can be approximated by substituting Eq. (2.5) and Eq. (2.6) into Eq. (2.4),
\[ H = - \sum_{(i,j)} J [M(\sigma_i + \sigma_j) - M^2] - \mu H \sum_{i}^N \sigma_i \]

\[ = \sum_{(i,j)} [-JM(\sigma_i + \sigma_j) + JM^2] - \mu H \sum_{i}^N \sigma_i \]

\[ = -JM \sum_{(i,j)} (\sigma_i + \sigma_j) + J \sum_{(i,j)} M^2 - \mu H \sum_{i}^N \sigma_i \]

\[ = \frac{1}{2} J \sum_{(i,i+1)} \sum_{i}^N M^2 - \frac{1}{2} JM \sum_{(i,i+1)} \sum_{i}^N (\sigma_i + \sigma_{i+1}) - \mu H \sum_{i}^N \sigma_i \]

(2.7)

where the factor of 1/2 is added to avoid double counting and \( \{i, i + 1\} \) represents the nearest neighbors at site \( i \). Because the system is transitional invariant, Eq. (2.7) can be simplified as

\[ H = \frac{1}{2} J d N M^2 - (JMd + \mu H) \sum_{i}^N \sigma_i \]

(2.8)

where \( d \) is the coordination number depending on the crystal structure.

According to the definition of the partition function, \( Z \),

\[ Z = \prod_{i=1}^N \left( \sum_{\sigma_i = \pm 1} e^{-\beta H} \right) \]

(2.9)

where \( \beta = 1/k_B T \) with \( k_B \) is the Boltzmann constant. The partition function of ferromagnets can be derived using Eq. (2.8) and Eq. (2.9),

\[ Z = \prod_{i=1}^N \left( \sum_{\sigma_i = \pm 1} e^{-\beta \left[ \frac{1}{2} J d N M^2 - (JMd + \mu H) \sum_{i}^N \sigma_i \right]} \right) \]
\[ Z = \{2 \cosh[\beta (Jd + \mu H)]\}^N e^{-\beta dNJM^2/2} \] (2.10)

The thermal expectation value of \( \langle \sigma_i \rangle \) can be calculated from the partition function by its definition,

\[ \langle \sigma_i \rangle = \frac{1}{Z} \prod_{i=1}^{N} \left( \sum_{\sigma_i = \pm 1} e^{-\beta \mathcal{H}} \right) \] (2.11)

where Eq. (2.11) can be rewritten as

\[
\langle \sigma_i \rangle = \frac{1}{Z} \prod_{i=1}^{N} \left[ \left( -\frac{1}{\mu} \right) \frac{\partial \mathcal{H}}{\partial \mu} e^{-\beta \mathcal{H}} \right] \\
= -\frac{1}{Z} \frac{1}{\mu} \prod_{i=1}^{N} \left[ \frac{\partial \mathcal{H}}{\partial \mu} \left( -\frac{1}{\beta} \right) \frac{\partial}{\partial \mathcal{H}} \left( e^{-\beta \mathcal{H}} \right) \right] \\
= \frac{1}{Z} \frac{1}{\mu \beta} \prod_{i=1}^{N} \left[ \frac{\partial \mathcal{H}}{\partial \mathcal{H}} \frac{\partial}{\partial \mathcal{H}} \left( e^{-\beta \mathcal{H}} \right) \right] \\
= \frac{1}{Z} \frac{1}{\mu \beta} \frac{\partial}{\partial \mathcal{H}} \prod_{i=1}^{N} \left( \sum_{\sigma_i = \pm 1} e^{-\beta \mathcal{H}} \right)
\]

Recall the definition of the partition function in Eq. (2.9), the above equation becomes

\[ \langle \sigma_i \rangle = \frac{1}{Z} \frac{1}{\mu \beta} \frac{\partial Z}{\partial \mathcal{H}} \]

\[ \Rightarrow \langle \sigma_i \rangle = \frac{1}{\mu \beta} \frac{\partial \ln Z}{\partial \mathcal{H}} \] (2.12)
By substituting Eq. (2.12) and Eq. (2.10) into Eq. (2.6), we can calculate the magnetization

\[
M = \frac{1}{N} \frac{1}{\mu \beta} \frac{\partial}{\partial H} \ln \{2 \cosh[\beta(JdM + H)]\} \left\{ \frac{\beta NJdM^2}{N} e^{\frac{\beta NJdM^2}{2}} \right\}
\]

\[
= \frac{1}{N} \frac{1}{\mu \beta} \frac{\partial}{\partial H} \left\{ N \ln 2 + N \ln[\cosh(\beta JdM + \beta H)] - \frac{1}{2} \beta NJdM^2 \right\}
\]

\[
\Rightarrow M = \tanh(\beta JdM + \beta H) \quad (2.13)
\]

Let \( H = 0 \), i.e., no external field applied, Eq. (2.13) is simplified

\[
M = \tanh(\beta JdM) \quad (2.14)
\]

Although there is no analytical solution to the above transcendental equation, it can be solved graphically by finding the intersections of the plots of both sides, as shown in Fig. 4. The case of \( \beta Jd \leq 1 \) corresponds to the diamagnetic state because the only solution of Eq. (2.14) is \( M = 0 \) which satisfies its orderliness description.

Figure 4. Graphical solution of the transcendental equation, \( \tanh(\beta JdM + \beta H\mu) = m \), for the magnetization of a ferromagnet.
There are three solutions, \( M = 0 \) and \( M = \pm M_0 \), in the case of \( \beta J d > 1 \). However, except for the self-constraint equation of the magnetization, the values of magnetization should also minimize the free energy by the requirement of equilibrium state. As shown in Fig. 5, the system will only be stable at \( M = \pm M_0 \) corresponding to the ferromagnetic state. In summary, the value of critical temperature, \( T_C \), is given by \( \beta J d = 1 \) where the system changes from a ferromagnetic state to a diamagnetic state.

\[
[k_B T_C = Jd] \tag{2.15}
\]

![Figure 5](image.png)

Figure 5. The plot of free energy vs. magnetization

The free energy, \( f \), is defined as

\[
f = - \frac{k_B T}{N} \ln Z \tag{2.16}
\]
Substituting Eq. (2.10) into Eq. (2.16), we get

\[ f = \frac{1}{2} J d M^2 - k_B T \ln[\cosh(\beta (J d M + H))] - k_B T \ln 2 \]  

(2.17)

For zero applied field, \( H = 0 \), applying the Taylor expansion near about \( M = 0 \), of the logarithm term gives

\[ f = \frac{1}{2} J d (1 - \beta J d) M^2 + \frac{1}{12} \beta^3 d^4 J^4 M^4 - k_B T \ln 2 \]  

(2.18)

Substituting Eq. (2.15) into Eq. (2.18), the free energy becomes

\[ f = \frac{1}{2} k_B T_c (T - T_c) M^2 + \frac{1}{12} k_B T_c^4 T^3 - k_B T \ln 2 \]  

(2.19)

Comparing Eq. (2.19) with Eq. (2.1), for ferromagnets, we get

\[ f_0(T) = -k_B T \ln 2 \]  

(2.20a)

\[ a_0(T) = \frac{1}{2} k_B T_c (T - T_c) \]  

(2.20b)

\[ b_0(T) = \frac{1}{12} k_B T_c^4 T^3 \]  

(2.20c)

Moreover, the coexistence curve of magnetization for \( H = 0 \) can be derived by expanding Eq. (2.13) near the critical point,

\[ M = \beta J d M - \frac{1}{3} (\beta J d M)^3 \]  

(2.21)

Substituting Eq. (2.15) into Eq. (2.21),
\[ M = \frac{T_c}{T} M - \frac{1}{3} \left( \frac{T_c}{T} M \right)^3 \]

\[ = \pm \sqrt{3} \left( \frac{T}{T_c} \right)^3 \left( \frac{T_c - T}{T} \right) \]

Using the approximation, \( T / T_c \approx 1 \), in the critical region to simplify the above equation,

\[ M = \pm \sqrt{3} t^{1/2} \]

(2.22)

where \( t = (T_c - T) / T_c \) is the reduced temperature.

It follows from Eq. (2.22) that magnetization is a function of only temperature, where \( M \sim t^{1/2} \), in the critical region implies that the critical behavior of magnetization is universal for all magnetic materials, including iron, nickel, cobalt, etc.

2.1.2. Liquid-Vapor Phase Transitions in Pure Fluids

For a fluid, the values of the gas phase and liquid phase molar volumes (or densities) are quite different below the critical temperature. As shown in Fig. 6, there is a step-change in molar volume between the gas and liquid phase. In this region, the gas phase and liquid phase are distinctly separated, \( i.e., \) the system is well ordered. Because the molar volume is different in these two coexisting phases, the system is translational asymmetrical. However, once the system reaches the critical temperature, both the discontinuity in the molar volume and the phase boundary vanish. Above the critical temperature, the system is completely disorganized because the two phases
merge into one phase. Moreover, the system now has translational symmetry due to the molar volume being independent of the locations.

Figure 6. Isotherms for van der Waals gas. The dashed curve is the coexistence curve

The continuous molar volume change at the critical point for pure fluids can be explained in the van der Waals gas model which includes the long-range attraction between molecules. The van der Waals gas equation of state for a gas is

\[ P = \frac{RT}{\bar{V} - b} + \frac{a}{\bar{V}^2} \]  

(2.23)

where \( P \) is the pressure, \( \bar{V} \) is the molar volume, and \( a \) and \( b \) are constants that depend on the substance.

In this section, we will not only show the universality of critical point phenomena in fluids but also prove that the critical point phenomenon in the van der Waals gas and the ferromagnets
are isomorphic. The first and second order derivatives of $P$ with respect to $\bar{V}$ satisfy the following conditions at the critical point,

$$
\left( \frac{\partial P}{\partial \bar{V}} \right)_{T=\bar{T}_c} = 0
$$

$$
\left( \frac{\partial^2 P}{\partial \bar{V}^2} \right)_{T=\bar{T}_c} = 0
$$

Substituting Eq. (2.23) into Eq. (2.24), we can get the values of critical pressure $P_c$, critical molar volume $\bar{V}_c$ and critical temperature $T_c$

$$
\bar{V}_c = 3b, \quad T_c = \frac{8a}{27Rb}
$$

The differential of the Helmholtz energy, $A$, is

$$
dA = -S \, dT - P \, d\bar{V}
$$

where $S$ is entropy. We define the molar free energy $\tilde{A} = A/n$, molar entropy $\tilde{S} = S/n$, and molar volume $\bar{V} = V/n$, where “$n$” is the number of moles. At the critical temperature, $T = \bar{T}_c$, the temperature is a constant, so Eq. (2.26) reads

$$
d\tilde{A} = -P \, d\bar{V}
$$

Substituting Eq (2.23) into Eq. (2.27) to get

$$
d\tilde{A} = -\frac{RT}{\bar{V} - b} \, d\bar{V} + \frac{a}{\bar{V}^2} \, d\bar{V}
$$
The integral of Eq. (2.29) is
\[
\tilde{A} = \tilde{A}^0 - RT \ln (\bar{V} - b) - \frac{a}{\bar{V}}
\]
(2.29)

where $\tilde{A}^0$ is a constant of integration.

Define
\[
\bar{V}_r = \frac{V}{V_c}
\]
(2.30)

Substituting Eq. (2.30) into Eq. (2.29), we get
\[
\tilde{A} = \tilde{A}^0 - RT \ln (\bar{V}_c \bar{V}_r - b) - \frac{a}{\bar{V}_c \bar{V}_r}
\]
(2.31)

At the critical temperature, the Helmholtz free energy is a function of $\bar{V}_r$, $\tilde{A} = \tilde{A} (\bar{V}_r)$. Let $\nu$ be a small deviation from $\bar{V}_r = 1$. At a temperature below the critical temperature, the molar volume of the liquid is $\bar{V}_r^L = 1 - \nu$ and the molar volume of the gas is $\bar{V}_r^G = 1 + \nu$. Obviously, $\nu$ equals zero above the critical temperature and acquires a nonvanishing value below the critical temperature. We shall assign $\nu$ as the order parameter of van der Waals gas, and construct the free energy as
\[
f (\nu) = \tilde{A} (\bar{V}_r^L) + \tilde{A} (\bar{V}_r^G) - 2 \tilde{A} (1)
\]
(2.32)

Substituting Eq. (2.29) and Eq. (2.30) into Eq. (2.32) to get
\[ f(v) = -RT[\ln(\bar{V}_c - \bar{V}_c v - b) + \ln(\bar{V}_c + \bar{V}_c v - b)] - \frac{a}{\bar{V}_c \left( \frac{1}{1-v} + \frac{1}{1+v} \right)} + 2RT_c \ln(\bar{V}_c - b) + \frac{2a}{\bar{V}_c} \]

Similarly, the above function can be expressed as the series expansion

\[ f(v) = \frac{2a}{3b} \left( \frac{1}{b} - \frac{3}{V_c} \right) + 2R[\ln(2b)T_c - \ln(\bar{V}_c - b) T] + \left[ \frac{RT\bar{V}_c^2}{(V_c - b)^2} - \frac{2a}{V_c} \right] v^2 \]

\[ + \left[ \frac{RT\bar{V}_c^4}{2(V_c - b)^4} - \frac{2a}{V_c} \right] v^4 \]

Substituting Eq. (2.25) into the above equation, we get

\[
\boxed{f(v) = -2R \ln(2b) (T - T_c) + \frac{9R}{4} (T - T_c) v^2 + \frac{81R}{32} \left( T - \frac{8}{9} T_C \right) v^4} \quad (2.33)
\]

Comparing Eq. (2.33) for the van der Waals gas with Eq. (2.1), we get

\[ f_0(T) = -2R \ln(2b) (T - T_c) \quad (2.34a) \]

\[ a_0(T) = \frac{9R}{4} (T - T_c) v^2 \quad (2.34b) \]

\[ b_0(T) = \frac{81R}{32} \left( T - \frac{8}{9} T_c \right) v^4 \quad (2.34c) \]

At the critical point, the derivative of free energy satisfies the following condition

\[
\frac{\partial f}{\partial v} = \frac{9R}{2} (T - T_c) v + \frac{81R}{8} \left( T - \frac{8}{9} T_c \right) v^3 = 0 \quad (2.35)
\]
Because the root \( v = 0 \) is trivial, we can solve Eq. (2.35)

\[
\frac{T - T_c}{T_c} + \frac{9}{16} \left( \frac{T}{T_c} - \frac{8}{9} \right) v^2 = 0
\]

If we employ the approximation, \( T/T_c \approx 1 \), in the critical region, to simplify the above equation, the result is

\[
v = \pm 2 t^{\frac{1}{2}}
\]

(2.36)

where we used the definition of the reduced temperature, \( t = (T_c - T)/T_c \).

Because by virtue of Eq. (2.36) the deviation in molar volume, in the van der Waals gas is only dependent on temperature near the critical point, the critical behavior is universal for all fluids, including helium, carbon dioxide, ethanol, etc. By comparing Eq. (2.33) with Eq. (2.19), one finds that the free energies in ferromagnets and the pure fluid share the same pattern. Moreover, the shapes of the coexistence curves, i.e., Eq. (2.22) and Eq. (2.36) both are power laws involving the exponent value, \( 1/2 \). The identical critical behavior between ferromagnets and pure fluids suggests that the critical point phenomenon is universal among different systems and the critical behavior is not dependent on the fine details of the system.

2.1.3. Liquid-Liquid Phase Transitions in Binary mixtures

In the last two sections, the universality of critical point phenomena exhibited by the one-component systems, ferromagnets and pure fluid, has been demonstrated. In this section, we will
examine the binary liquid mixture and show that the universality of critical phenomena is not limited to one-component systems. In the case of a binary liquid mixture, two liquids are immiscible on the concave side of the coexistence curve (CXC), whereas they are miscible on the convex side, and the critical point is at the extremum of the CXC. At the critical point, the two liquid phases mix, and the composition of the system is uniform and symmetrical. Just as the ideal gas model cannot explain the critical point in the pure fluid, the ideal mixture model does not manifest a phase transition and a critical point. We thus invoke the regular solution model to interpret the critical point in a binary liquid mixture.

In the regular solution model, the molar entropy of mixing, $\Delta \bar{S}_{mix}$, is equal to that of an ideal solution,

$$\Delta \bar{S}_{mix} = -R(x_1 \ln x_1 + x_2 \ln x_2)$$

but the molar enthalpy of mixing, $\Delta \bar{H}_{mix}$, is nonzero and defined as [34]

$$\Delta \bar{H}_{mix} = \xi x_1 x_2$$

where $\xi$ is the parameter that represents the interactions between components.

Hence, the Gibbs free energy of mixing per mole is

$$\Delta \tilde{G}_{mix} = \Delta \bar{H}_{mix} - T \Delta \bar{S}_{mix} = RT(x_1 \ln x_1 + x_2 \ln x_2) + \xi x_1 x_2$$

According to the second law, the equilibrium state in the binary mixture corresponds to the state of minimal free energy of mixing and, hence, is determined by

$$\frac{\partial \Delta \tilde{G}_{mix}}{\partial x_1} = 0$$
\[
\frac{\partial^2 \Delta \bar{G}_{\text{mix}}}{\partial x_1^2} > 0 
\] (2.41)

The solution of Eq. (2.41) is

\[
\ln \left( \frac{x_1}{1 - x_1} \right) = \frac{\xi}{2RT} (2x_1 - 1) 
\] (2.42)

Because Eq. (2.42) is a transcendental equation, like the corresponding result for the magnetization given by Eq. (2.14), it can only be solved graphically. The solutions to Eq. (2.42) are plotted in Fig. 7.

Figure 7. Graphical solution of the self-constraint equation of molar fraction of a binary mixture.

The schematic behavior \(\partial^2 \Delta \bar{G}_{\text{mix}}/\partial x_1^2\) is sketched in Fig. 8, which shows that there are two minima of the free energy for \(T < 2\xi/R\). These two minima will start to approach each other on heating until finally at \(T = 2\xi/R\) they become identical. It illustrates that the system with a temperature lower than \(2\xi/R\) will separate into two phases with compositions corresponding to
the two minima forming spontaneously. When the temperature is higher than $2\xi/R$, the phase boundary will vanish, and the two phases will merge into one homogenous phase.

![Figure 8. Schematic behavior of $\partial^2 \Delta \tilde{G}_{mix}/\partial x_1^2$ for three different temperatures.](image)

The critical point, therefore, corresponds to the minimum of the $\partial^2 \Delta \tilde{G}_{mix}/\partial x_1^2$ curve and, hence, is determined by

$$\frac{\partial^2 \Delta \tilde{G}_{mix}}{\partial x_1^2} = \frac{\partial^3 \Delta \tilde{G}_{mix}}{\partial x_1^3} = 0 \quad (2.43)$$

Because the mole fractions in the binary mixture stratify

$$x_1 + x_2 = 1 \quad (2.44)$$

The values of critical composition and critical temperature can be easily calculated using Eq. (2.39), Eq. (2.43), and Eq. (2.44). One finds,

$$x_c = \frac{1}{2}, \quad T_c = \frac{2\xi}{R} \quad (2.45)$$
The small deviation from the critical composition, $\epsilon$, is assigned the role of the order parameter in the binary mixture. For the mole fractions in each liquid,

$$x_1 = \frac{1}{2} - \epsilon \quad (2.46a)$$

$$x_2 = \frac{1}{2} + \epsilon \quad (2.46b)$$

Put Eqs. (2.46) into Equation (2.39) to get

$$\Delta \tilde{G}_{mix} = \frac{RT}{2} \left[ (1 - 2\epsilon) \ln \left( \frac{1}{2} - \epsilon \right) + (1 + 2\epsilon) \ln \left( \frac{1}{2} + \epsilon \right) \right] + \frac{\xi}{2} \left( \frac{1}{2} - \epsilon \right) \left( \frac{1}{2} + \epsilon \right) \quad (2.47)$$

In the vicinity of the critical point, the order parameter, $\epsilon$, is small enough to expand Eq. (2.47) in a Taylor series

$$\Delta \tilde{G}_{mix} = (2RT - \xi)\epsilon^2 + \frac{4}{3}RT\epsilon^4 - RT \ln 2 + \frac{\xi}{4} \quad (2.48)$$

Substituting Eq. (2.45) into the above equation,

$$\Delta \tilde{G}_{mix} = 2RT \left( T - T_c \right)\epsilon^2 + \frac{4}{3}RT\epsilon^4 - RT \ln 2 + \frac{RT_c}{2} \quad (2.49)$$

The function of the coexistence curve for the binary mixture can be derived by solving the condition of equilibrium state, $\partial \Delta \tilde{G}_{mix} / \partial \epsilon = 0$,

$$\frac{\partial \Delta \tilde{G}_{mix}}{\partial \epsilon} = 4RT \left( T - T_c \right)\epsilon + \frac{16}{3}RT\epsilon^3 = 0$$

One root is $\epsilon = 0$ which is trivial. The non-trivial roots are

$$\epsilon = \pm \frac{\sqrt{3}}{2} t^{1/2} \quad (2.50)$$
The temperature dependence of the order parameter $\epsilon$ is independent of the substance constant $\xi$ at the critical point implies that the critical behaviors of all binary mixtures are identical. The exponent in Eq. (2.50) is the same as the exponents in Eq. (2.22) and Eq. (2.36). This implies that similar patterns of the free energy suggest that the critical phenomenon in binary mixtures is isomorphic to that of ferromagnets and pure fluids.

When the order parameter $\psi$ is properly selected, the free energy $f(\psi)$ of different systems can be reformed in similar patterns at the critical point. The order parameter at the critical point is a function of only temperature and is independent of the nature of the system. The universality of the critical phenomena is implied by the same exponent of the three distinct systems. The exponents characterizing critical behavior for thermodynamic properties are the so-called critical exponents. A list of the critical exponents and their theoretical and experimental values is presented in Table. 3.

<table>
<thead>
<tr>
<th>Critical exponent</th>
<th>Theoretical Value</th>
<th>Experimental value [22]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$</td>
<td>0</td>
<td>$0.10 \pm 0.05$</td>
</tr>
<tr>
<td>$\beta$</td>
<td>$1/2$</td>
<td>$0.32 \pm 0.01$</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>1</td>
<td>$1.24 \pm 0.05$</td>
</tr>
<tr>
<td>$\delta$</td>
<td>3</td>
<td>$4.8 \pm 0.2$</td>
</tr>
</tbody>
</table>

Although Landau’s theory gives a phenomenological description of the phase transition and a plausible explanation of the universality of the critical phenomena, it fails to give the accurate values of critical exponents, because the free energy is a nonanalytical function at the critical point at which the Taylor series should not be applied. Table. 3 shows that the difference between theoretical and experimental values of the critical exponents is considerable. As the system approaches the critical point, the fluctuation which is ignored in the mean-field approximation
increases causing the free energy to be a non-analytical function; hence, the Taylor expansion used in Landau’s theory is invalid. Landau’s theory was corrected by K. Wilson who was able to calculate much more accurate values of the critical exponents $\alpha, \beta, \gamma, \delta$ by summing the partition function using the renormalization group theory [35].

2.2. The Scaling Property of Critical Point Phenomena

Although Landau’s theory fails to give the quantitative prediction of critical behavior, there are some same relationships in the mean-field values for the critical exponents that are also valid in the case of the experimental values. The connection between the critical exponents has its origin in the scaling property of critical point phenomena. Instead of calculating the precise values by using the renormalization group theory which requires a huge computational effort, the relationships between the critical exponents can be derived by assuming the free energy is a generalized homogeneous function in the critical region. A generalized homogeneous function is defined as

$$\lambda f(x_1, x_2, \ldots, x_n) = f(\lambda^{a_1}x_1, \lambda^{a_2}x_2, \ldots, \lambda^{a_n}x_n)$$

(2.51)

The goal is to find expressions for the empirical exponents $\alpha, \beta, \gamma, \delta$ in terms of the scaling powers $\{a_i\}$. For the binary mixture, the scaling property of critical point phenomena can be derived in the grand canonical ensemble. The grand potential of the grand canonical ensemble, $\phi_G$, is defined by

$$\phi_G = E - TS - \mu n$$

(2.52)
where $E$ is the internal energy and $n$ is the number of moles. Given the Gibbs equation

$$dE = TdS - PdV + \mu dn$$

the total differential of Eq. (2.52) is

$$d\phi_G = -SdT - PdV - nd\mu$$

If the system is incompressible, $dV = 0$, and the above equation becomes

$$d\phi_G = -SdT - nd\mu$$

the grand potential can be rewritten as a function of reduced variables $\phi_G(t, \mu)$ which are defined by

$$t = \frac{|T - T_c|}{T_c}$$

$$\mu = \frac{|\mu_1 - \mu_c|}{\mu_c}$$

where $\mu_1$ is the chemical potential of component 1, $\mu_c$ is the chemical potential at the critical point.

The grand potential $\phi_G(t, \mu)$ is assumed to be a generalized homogeneous function at the critical point by the scaling hypothesis.

$$\lambda \phi_G(t, \mu) = \phi_G(\lambda^a t, \lambda^{a\kappa} \mu)$$

### 2.2.1. Isochoric Heat Capacity $C_V \sim t^{-\alpha}$

The heap capacity, $C_V$, is defined by
\[ C_V = T \left( \frac{\partial S}{\partial T} \right)_V \]  

(2.56)

The total differential of Eq. (2.52) is

\[ d\phi_G = \left( \frac{\partial \phi_G}{\partial T} \right)_T dT + \left( \frac{\partial \phi_G}{\partial \mu} \right)_\mu d\mu \]  

(2.57)

A comparison of Eq. (2.57) with Eq. (2.53) gives

\[ S = -\left( \frac{\partial \phi_G}{\partial T} \right)_T \]  

(2.58)

Substitution Eq. (2.58) into Eq. (2.56) has the result

\[ C_V = -T \left( \frac{\partial^2 \phi_G}{\partial T^2} \right)_{T,V} \]  

Based on the above equation, the heat capacity can be reformed to a function of reduced temperature as

\[ C_V = -\frac{T}{T_C^2} \left( \frac{\partial^2 \phi_G}{\partial t^2} \right)_V \]  

(2.59)

By taking the second order of partial derivative on both sides of Eq. (2.55) with respect to \( t \),

\[ \lambda \frac{\partial \phi_G(t, \mu)}{\partial t} = \frac{d(\lambda^a \cdot t)}{dt} \left( \frac{\partial^2 \phi_G(\lambda^a \cdot t, \lambda^a \cdot \mu)}{\partial (\lambda^a \cdot t)^2} \right)_\mu \]

\[ \lambda \frac{\partial \phi_G(t, \mu)}{\partial t} = \lambda^a \cdot \left( \frac{\partial^2 \phi_G(\lambda^a \cdot t, \lambda^a \cdot \mu)}{\partial (\lambda^a \cdot t)^2} \right)_\mu \]

\[ \lambda \frac{\partial^2 \phi_G(t, \mu)}{\partial t^2} = \lambda^a \cdot \frac{d(\lambda^a \cdot t)}{dt} \cdot \left( \frac{\partial^2 \phi_G(\lambda^a \cdot t, \lambda^a \cdot \mu)}{\partial t^2} \right)_\mu \]
\[
\lambda \frac{\partial^2 \phi_G(t, \mu)}{\partial t^2} = \lambda^{2a_t} \left( \frac{\partial \phi_G(\lambda^{a_t}t, \lambda^{a_u} \mu)}{\partial \lambda^{a_t}t} \right)_{\mu}
\]

\[
\frac{\partial^2 \phi_G(t, \mu)}{\partial t^2} = \lambda^{2a_t-1} \frac{\partial^2 \phi_G(\lambda^{a_t}t, \lambda^{a_u} \mu)}{\partial (\lambda^{a_t}t)^2}
\]

\[
-\frac{T}{T_C^2} \frac{\partial^2 \phi_G(t, \mu)}{\partial t^2} = -\lambda^{2a_t-1} \frac{T}{T_C^2} \frac{\partial^2 \phi_G(\lambda^{a_t}t, \lambda^{a_u} \mu)}{\partial (\lambda^{a_t}t)^2}
\]

and substituting Eq. (2.59) into the above equation,

\[
C_V(t, \mu) = \lambda^{2a_t-1} C_V(\lambda^{a_t}t, \lambda^{a_u} \mu)
\]  

(2.60)

because Eq. (2.6) is valid for all values of \( \lambda \) including

\[
\lambda^{a_t} t = 1
\]  

(2.61)

Eq. (2.60) becomes

\[
C_V(t, \mu) = t^{\frac{1-2a_t}{a_t}} C_V(1, \lambda^{a_u} \mu)
\]

At the critical equilibrium \( \mu = 0 \), the above equation becomes

\[
C_V(t, 0) = t^{\frac{1-2a_t}{a_t}} C_V(1,0)
\]

Near the critical point, the critical behavior of heat capacity is characterized by

\[
C_V = A^{\pm} t^{-\alpha}
\]

Therefore, the value of \( \alpha \) is given by

\[
\alpha = -\frac{1-2a_t}{a_t}
\]  

(2.62)
2.2.2. Coexistence Curve $x \sim t^\beta$

A comparison of Eq. (2.53) with Eq. (2.57) also gives

$$n = -\left(\frac{\partial \phi_G}{\partial \mu}\right)_{T,Y}$$

Similarly, by taking the first order of partial derivative on both sides of Eq. (2.55) with respect to $\mu$, we get

$$n(t, \mu) = \lambda a^{1-a} n(\lambda a t, \lambda a \mu)$$ (2.63)

At the critical point where $t = 0$, $\mu = 0$, and the critical value of $n$ is $n_c$

$$n_c = \lambda a^{1-a} n(0,0)$$ (2.64)

Subtracting Eq. (2.64) from Eq. (2.63)

$$n(t, \mu) - n_c = \lambda a^{1-a} n(\lambda a t, 0) - \lambda a^{1-a} n_c$$ (2.65)

At the critical equilibrium $\mu = 0$, the above equation becomes

$$n(t, 0) = \lambda a^{1-a}[n(\lambda a t, 0) - n_c] + n_c$$ (2.66)

Substituting Eq. (2.61) into Eq. (2.66)

$$n(t, 0) = t \frac{1-a}{a t} [n(1,0) - n_c] + n_c$$ (2.67)

Dividing both sides of the above equation by the total number of moles,

$$x(t, 0) = t \frac{1-a}{a t} [x(1,0) - x_c] + x_c$$ (2.67)
Comparing Eq. (2.50) with Eq. (2.67) gives the value of the critical exponent $\beta$,

$$
\beta = \frac{1 - a_\mu}{a_t}
$$

(2.68)

2.2.3. Response Function $\chi \sim t^{-\gamma}$

The response function describes the order parameter response to an applied field, such as the magnetic susceptibility for magnetic materials and the compressibility for pure fluids. The magnetic susceptibility, $\chi_T$, is expressed as

$$
\chi_T = \left(\frac{\partial M}{\partial H}\right)_T
$$

(2.69)

The magnetization is given by the partial derivative of free energy with respect to the applied field,

$$
M = -\left(\frac{\partial f}{\partial H}\right)_T
$$

(2.70)

Combining Eq. (2.69) and Eq. (2.70), magnetic susceptibility is the second derivative of free energy

$$
\chi_T = -\left(\frac{\partial^2 f}{\partial H^2}\right)_T
$$

Likewise, the response function of a regular solution, $\mathcal{K}$, is defined by

$$
\mathcal{K} = -\left(\frac{\partial n}{\partial \mu}\right)_T = -\left(\frac{\partial^2 \phi_G}{\partial \mu^2}\right)_T
$$

(2.71)
The critical exponent of Eq. (2.71) can be derived by differentiating both sides of Eq. (2.63)

\[
\frac{\partial n(t, \mu)}{\partial \mu} = \lambda^{a_{\mu} - 1} \frac{\partial n(\lambda^{a_{t}} t, \lambda^{a_{\mu}} \mu)}{\partial \mu}
\]

Substituting Eq. (2.71) into the above equation, we have

\[
\chi(t, \mu) = \lambda^{2a_{\mu} - 1} \chi(\lambda^{a_{t}} t, \lambda^{a_{\mu}} \mu)
\]

Again, let \( \lambda^{a_{t}} t = 1 \) for the above equation,

\[
\chi(t, \mu) = t^{\frac{1 - 2a_{\mu}}{a_{t}}} \chi(1, \lambda^{a_{\mu}} \mu)
\]

At the critical equilibrium \( \mu = 0 \), the response function is

\[
\chi(t, \mu) = t^{\frac{1 - 2a_{\mu}}{a_{t}}} \chi(1, 0)
\]

The critical exponent characterizes the response function in the critical region is defined by

\[
\chi(t, \mu) = t^{-\gamma} \chi(1, 0)
\]

Therefore, the critical exponent \( \gamma \) is given by

\[
\gamma = -\frac{1 - 2a_{\mu}}{a_{t}}
\]

2.2.4. Critical Isotherm \( \mu \sim x^\delta \)

The isotherm at the critical temperature, \( t = 0 \), is characterized by
\( \mu \sim x^\delta \)  \hfill (2.73)

The equation of \( \delta \) can be derived by setting \( \lambda = \frac{1}{\mu^{a_\mu}} \) in Eq. (2.65). The result is

\[
x(t, v, \mu) = \mu^{a_\mu} \frac{1-a_\mu n_c - n(\lambda^{a_\mu} t, 1)}{n(0,0)}
\]

Along the critical isotherm

\[
x(t, \mu) = \mu^{a_\mu} \frac{1-a_\mu n_c - n(0,1)}{n_c} \tag{2.74}
\]

A comparison of Eq. (2.74) with Eq. (2.73) gives

\[
\delta = \frac{1 - a_\mu}{a_\mu} \tag{2.75}
\]

By combing Eq. (2.62), Eq. (2.68), Eq. (72), and Eq. (2.75), one can prove the following critical exponent identities

\[
\beta(\delta - 1) = \gamma \sim \text{Widom identity}
\]

\[
\alpha + \beta(1 + \delta) = 2 \sim \text{Griffiths identity}
\]

\[
\alpha + 2\beta + \gamma = 2 \sim \text{Rushbrook identity}
\]

These relations are called scaling laws. The scaling laws derived from regular solutions are equivalent to those from magnets and pure fluids although different variables may be chosen in the derivation. [36] Despite the fact that scaling laws are based on an unproved assumption, the prediction of the scaling laws is in excellent agreement with the experimental values. Instead of numerical values, the scaling laws give functional relations among the critical exponents and thus limit the number of independent critical exponents.
2.3. The Classification of the Critical Behavior

The critical behaviors are classified into two categories: the weak singularities are characterized by critical exponents $\alpha$ or $\beta$, and the strong singularities are characterized by critical exponents $\gamma$ or $\delta$. Griffiths and Wheeler analyze the geometrical distinction between the quantities with weak singularities and those with strong singularities; hence, they determine whether or not a quantity diverges strongly or weakly depending upon the path of approach to the critical point. Along a path asymptotically parallel to the coexistence curve, such as $C_V \sim t^{-\alpha}$ for a pure fluid, the quantity has a weak divergence at the critical point. If the direction of approach to the critical point makes an angle with the coexistence curve, such as $\kappa_T \sim t^{-\gamma}$ for a pure fluid, the quantity will have a strong divergence, as shown in Fig. 9.

![Liquid-vapor coexistence curve and critical point for a pure fluid](image)

Figure 9. Liquid-vapor coexistence curve and critical point for a pure fluid
For a system with \( F \) independent intensive variables, Griffiths and Wheeler divided the variables into two classes: the field variables, \( h \), like temperature and pressure, their values are the same for different phases. In contrast to field variables, the “density” variables, like the density itself, \( \rho \), have values that differ in each coexisting phase. Ordinarily, a density variable, \( \rho_i \), is determined by differentiating the free energy, \( f \), with respect to its conjugated field variable, \( h_i \).

\[
\rho_i = -\frac{\partial f}{\partial h_i} \tag{2.76}
\]

In the critical region, a thermodynamic property that diverges can be expressed as the derivative of a density variable with respect to a field variable,

\[
\frac{\partial \rho_i}{\partial h_j} = -\frac{\partial^2 f}{\partial h_i \partial h_j} \tag{2.77}
\]

Hence, both strong and weak divergences are included in the \( m \times m \) Jacobian determinant,

\[
J = \frac{\partial (\rho_1, \rho_2, \ldots, \rho_m)}{\partial (h_1, h_2, \ldots, h_m)} = \begin{bmatrix}
\frac{\partial \rho_1}{\partial h_1} & \ldots & \frac{\partial \rho_1}{\partial h_m} \\
\vdots & \ddots & \vdots \\
\frac{\partial \rho_m}{\partial h_1} & \ldots & \frac{\partial \rho_m}{\partial h_m}
\end{bmatrix} = \begin{bmatrix}
\frac{\partial^2 f}{\partial h_1^2} & \ldots & \frac{\partial^2 f}{\partial h_m^2} \\
\vdots & \ddots & \vdots \\
\frac{\partial^2 f}{\partial h_1 \partial h_m} & \ldots & -\frac{\partial^2 f}{\partial h_m^2}
\end{bmatrix} \tag{2.78}
\]

In the case of \( m = 1 \), the determinant of matrix (2.78), \( D(h_1) \), is

\[
D(h_1) = \frac{\partial \rho_1}{\partial h_1} = -\frac{\partial^2 f}{\partial h_1^2} \tag{2.79}
\]
In most cases, $D(h_1)$ diverges strongly at the critical point unless $h_1$ is parallel to the coexistence curve. In that case, $D(h_1)$ diverges weakly at the critical point.

In the case of $m = 2$, the determinant of matrix (2.78) is expressed as

$$
D(h_1, h_2) = \begin{vmatrix}
\frac{\partial^2 f}{\partial h_1^2} & \frac{\partial^2 f}{\partial h_1 \partial h_2} \\
\frac{\partial^2 f}{\partial h_1 \partial h_2} & \frac{\partial^2 f}{\partial h_2^2}
\end{vmatrix}
$$

(2.80)

Since the Helmholtz free energy for a pure fluid is expressed as

$$
dA = -SdT - VdP
$$

where $n$ is the total number of moles, the field variables, $\{h_i\}$, and their conjugate densities, $\{\rho_i\}$, are defined by

$$
h_1 = P; \ h_2 = T; \ \rho_1 = \bar{V} = V/n; \ \rho_2 = \bar{S} = S/n
$$

Eq. (2.80) for a pure fluid is expressed as

$$
D(P,T) = \begin{vmatrix}
\frac{\partial^2 \bar{A}}{\partial P^2} & \frac{\partial^2 \bar{A}}{\partial P \partial T} \\
\frac{\partial^2 \bar{A}}{\partial T \partial P} & \frac{\partial^2 \bar{A}}{\partial T^2}
\end{vmatrix} = \begin{vmatrix}
\frac{\partial V}{\partial P} & \frac{\partial V}{\partial T} \\
\frac{\partial S}{\partial P} & \frac{\partial S}{\partial T}
\end{vmatrix}_P
$$

The determinant, $D(P,T)$, of the above matrix is given by
\[ D(P, T) = \left( \frac{\partial V}{\partial P} \right)_T \left( \frac{\partial S}{\partial T} \right)_p - \left( \frac{\partial V}{\partial T} \right)_p \left( \frac{\partial S}{\partial P} \right)_T \]
\[ = \left( \frac{\partial V}{\partial P} \right)_T \left( \frac{\partial S}{\partial T} \right)_p - \left( \frac{\partial P}{\partial P} \right)_T \left( \frac{\partial V}{\partial T} \right)_p \left( \frac{\partial S}{\partial P} \right)_T \]
\[ = \left( \frac{\partial V}{\partial P} \right)_T \left[ \left( \frac{\partial S}{\partial T} \right)_p - \left( \frac{\partial P}{\partial T} \right)_p \left( \frac{\partial S}{\partial P} \right)_T \right] \]
\[ = \left( \frac{\partial V}{\partial P} \right)_T \left[ \left( \frac{\partial S}{\partial T} \right)_p - \left( \frac{\partial S}{\partial T} \right)_p \left( \frac{\partial V}{\partial P} \right)_T \right] \]
\[ \Rightarrow D(P, T) = \frac{\bar{V}}{\bar{T} \kappa_T C_V} \] (2.81)

where the following elementary thermodynamic relations are used.

\[ \kappa_T = \frac{1}{\bar{V}} \left( \frac{\partial V}{\partial P} \right)_T, \quad C_p = T \left( \frac{\partial S}{\partial T} \right)_p, \quad C_p - C_V = T \left( \frac{\partial V}{\partial T} \right)_p \left( \frac{\partial S}{\partial V} \right)_T \]

Because the critical exponents of \( C_V \) and \( \kappa_T \) are \( \alpha \) and \( \gamma \), respectively, the divergence of \( D(T, P) \) is so-called “strongly times weakly” with the exponent \( (\alpha + \gamma) \).

In the case of \( m \geq 3 \), if one density, \( \rho_j \), is fixed, the derivative of a density \( \rho_i \) with a field \( h_k \) can be expressed in Jacobian form as

\[ \left( \frac{\partial \rho_i}{\partial h_k} \right)_{\rho_j} = \frac{\partial (\rho_i, \rho_j)}{\partial (h_k, \rho_j)} = \frac{\partial (\rho_i, \rho_j)}{\partial (h_k, \rho_j)} \frac{\partial (h_k, \rho_j)}{\partial (h_k, \rho_j)} = \frac{D(h_i, h_j)}{D(h_j)} \] (2.82a)
In a situation where two densities held constant, the derivative of a density $\rho_i$ is expressed as

$$\left( \frac{\partial \rho_i}{\partial h_k} \right)_{\rho_j \rho_l} = \frac{\partial (\rho_i, \rho_j, \rho_l)}{\partial (h_k, h_j, h_l)} \frac{\partial (h_k, \rho_j, \rho_l)}{\partial (h_k, h_j, h_l)} = \frac{D(h_i, h_k, h_j)}{D(h_k, h_j)} \quad (2.82b)$$

There are three possible divergent behaviors of $D(X)/D(Y)$ which depend on the divergent behavior of the numerator and denominator: (1) if $D(X)$ is strongly times weakly divergent and $D(Y)$ is weakly divergent, then $D(X)/D(Y)$ is strongly divergent. (2) if $D(X)$ is strongly times weakly divergent and $D(Y)$ is strongly divergent, then $D(X)/D(Y)$ is weakly divergent. (3) if $D(X)$ and $D(Y)$ diverge in the same degree, then $D(X)/D(Y)$ is finite. Consequently, $(\partial \rho_i/\partial h_l)_{\rho_j}$ is weakly divergent if the field $h_l$, which is conjugated to the fixed density, $\rho_l$, is parallel to the coexistence curve, while $(\partial \rho_i/\partial h_l)_{\rho_j \rho_k}$ is finite at the critical point.

The geometrical characterization of thermodynamics at the critical point implies that the divergence behavior is dependent on the number of fixed densities. The derivative $(\partial \rho_i/\partial h_j)_{(\rho_k)}$ is strongly divergent with an empty set $\{\rho_k\}$. If there is one fixed density, $(\partial \rho_i/\partial h_j)_{(\rho_k)}$ is weakly divergent. Otherwise, $(\partial \rho_i/\partial h_j)_{(\rho_k)}$ will be finite at the critical point.
2.4. A Generalized Phase Rule Analysis of Critical Phenomena

The prediction of the critical behavior requires the knowledge of the number of fixed density variables in the system. However, the determination of the independent variables in the multicomponent system, especially with chemical reactions involved, is problematic due to the interactions between components related to each other.

The Gibbs phase rule was modified by V.J. Lee into a generalized form to find the number of independent variables for the heterogeneous chemical systems. [31] In the case of a critical point, the generalized phase rule is used to enumerate the independent thermodynamic variables held fixed, therefore, and to predict the divergence behavior of a particular derivative of a density with respect to a field in the case of a multicomponent system.

In the case of heterogeneous chemical systems, the number of independent intensive variables, \( F \), can be calculated from the generalized Gibbs phase rule. First, the \( R \) independent chemical reactions in the system are

\[
\sum_{j=1}^{C} \alpha_{ji}A_j = 0 \quad i = 1,2,\ldots,R
\]

(2.83)

where \( C \) is the number of chemical species, \( \alpha_{ji} \) is the stoichiometric coefficient of chemical species \( A_j \) in the \( ith \) chemical reaction. In the above equation, if \( \alpha_{ji} = 0 \), the species \( A_j \) is inert in the \( ith \) reaction; if \( \alpha_{ji} > 0 \), the species \( A_j \) is the product of the \( ith \) reaction; if \( \alpha_{ji} < 0 \), the species \( A_j \) is the reactant of the \( ith \) reaction. At equilibrium, the chemical potentials, \( \mu_j \), satisfy the relationship
\[
\sum_{j=1}^{c} \alpha_{ij} \mu_j = 0 \quad i = 1, 2, ..., R
\] (2.84)

For heterogeneous phase equilibrium with reactive species, there are \(C_k\) chemical species in the \(kth\) phase. By considering the possibility that some of the \(C_k\) species in the \(kth\) phase may also exist simultaneously in other phases, we define \(M_k\) as the number of species that exist simultaneously in any \(k\) phases. Hence

\[
C = \sum_{k=1}^{\phi} M_k
\] (2.85)

and

\[
\sum_{k=1}^{\phi} C_k = \sum_{k=1}^{\phi} kM_k = \sum_{k=1}^{\phi} M_k + \sum_{k=1}^{\phi} (k - 1)M_k
\] (2.86)

where \(\phi\) is the number of coexisting phases at chemical and phase equilibrium.

In addition to the \(R\) chemical potential relations, we shall also consider the equilibrium relations among phases; for those species which exist simultaneously in \(k\) phases, there are \((k - 1)M_k\) equations of equilibrium. The total number of equations of this type is

\[
\sum_{k=1}^{\phi} (k - 1)M_k
\]
For thermal equilibrium, \( i.e., T_1 = T_2 = \cdots = T_\phi \), there are \((\phi - 1)\) equilibrium equations. Similarly, for mechanical equilibrium, \( i.e., P_1 = P_2 = \cdots = P_\phi \), there also are \((\phi - 1)\) equilibrium equations. Therefore, the total number of equilibrium equations, \(N\), is

\[
N = R + 2(\phi - 1) + \sum_{k=1}^{\phi} (k - 1)M_k
\]  

(2.87)

Because of the chemical reactions and other conditions, the \(C_k\) species in the \(kth\) phase may not be completely independent. Let there be \(I_k\) invariant constraints due to stoichiometric and other conditions. The actual number of independent variable components of the \(kth\) phase equals \(C_k - I_k\). Furthermore, since only intensive variables, such as mole fraction, mole ratio, or weight percentage, describe the phase equilibrium, the sum in each phase must be unity. Hence, in the \(kth\) phase, there are only \(C_k - I_k - 1\) variables. Including the temperature and pressure, the \(kth\) phase is described by \(C_k - I_k + 1\) variables. Thus, the total number of variables is

\[
\sum_{k=1}^{\phi} (C_k - I_k + 1) = \sum_{k=1}^{\phi} C_k - \sum_{k=1}^{\phi} I_k + \phi
\]  

(2.88)

The degree of freedom, \(F\), of a heterogeneous system at chemical equilibrium is defined as the difference between the total number of variables and the total number of equilibrium equations. Combining Eqs. (2.86), (2.87), and (2.88), we get the generalized Gibbs phase rule

\[
F = C - \phi - R - \sum_{k=1}^{\phi} I_k + 2
\]  

(2.85)
In a liquid mixture where the values of $F$ independent intensive variables must be known, two of these are temperature and pressure; the remaining $F - 2$ variables must be densities. If the derivative of a density with respect to a field is going to diverge at a critical point, only one density can be fixed. Hence critical effects are not expected in multicomponent mixtures where $F > 3$. 
CHAPTER 3 THE REGULAR SOLUTION MODEL FOR MULTICOMPONENT SYSTEMS

Although there are numerous components in the binary mixture when an additional solute is included, the independent variables are limited by the phase rule. Those multicomponent systems, where the divergence behavior was observed at the critical endpoint, may be treated as a ternary mixture. In this chapter, the regular solution model is used to study the effect of added substances on the critical phenomena in the ternary mixture. Also, the divergence behaviors in the ternary mixture had been analyzed by the Griffiths-Wheeler rule.

3.1 Critical Points in Ternary Systems

The addition of a third component to a binary mixture increases the number of degrees of freedom from three to four. The result is a four-dimensional phase diagram which is difficult to visualize. Moreover, the critical point of binary mixtures at constant pressure becomes the critical curve of ternary mixtures. The description of global phase diagrams for the three-component and the four-component system are given by Griffiths, et al. [37]. Griffiths categorizes the critical points in ternary mixtures as critical end points and tri-critical points: At the critical end point, two
coexisting phases become identical while coexisting with the third phase, as shown in Fig. 10. At the tri-critical point, all three coexisting phases merged into one homogeneous phase simultaneously. The singularity behaviors at the critical end point in a binary mixture were predicted by Fisher [38] and observed by Wilding [39].

Figure 10. Schematic illustration of critical end points. Three phases are present in a closed tube (left) separated by two meniscuses. At the critical endpoint, the two phases become identical in the presence of the third phase (right) and this is illustrated in right by drawing the meniscus which has just vanished or is just about to vanish as a dashed line.

Upon addition of component 3 into a binary mixture of components 1 and 3, the composition of the ternary mixture is specified by mole fractions

\[
x_i = \frac{n_i}{\sum_{i=1}^{3} n_i}
\]

Because all experiments were carried out along the critical isopleth of the binary mixture, the ratio of \( n_1 \) and \( n_2 \)

\[
x = \frac{n_1}{n_2} = \frac{x_1}{x_2}
\]
is a constant, independent of any changes in the position of equilibrium. The mole fractions also satisfy the sum condition,

\[ x_1 + x_2 + x_3 = 1 \]

We thus obtain

\[ x_1 = \frac{x(1 - x_3)}{1 + x} \]

\[ x_2 = \frac{(1 - x_3)}{1 + x} \]

Therefore, the composition of the ternary mixture can be expressed in terms of one intensive composition variable \( x_3 \). The remaining two intensive variables are temperature, \( T \), and pressure, \( P \).

In the regular solution model, the Gibbs free energy of mixing per mole is given by

\[ \tilde{G}_{\text{mix}} = RT(x_1 \ln x_1 + x_2 \ln x_2 + x_3 \ln x_3) + \xi_{12}x_1x_2 + \xi_{13}x_1x_3 + \xi_{23}x_2x_3 \]

The condition for a critical point in a ternary mixture can be expressed as [40]

\[
\begin{vmatrix}
    G_{11} & G_{12} \\
    G_{12} & G_{22}
\end{vmatrix} = 0
\]

\[
\begin{vmatrix}
    \frac{\partial D}{\partial x_1} & \frac{\partial D}{\partial x_2}
\end{vmatrix} = 0
\]

where the shorthand notation \( G_{ij} = \partial^2 \tilde{G}_{\text{mix}} / (\partial x_i \partial x_j) \) has been used.
It’s difficult to calculate the critical point in a ternary regular solution; however, the slope of the critical curve on which the set of liquid-liquid equilibrium critical points lie may be evaluated. The critical line of the ternary mixture is on surface $S_1$ which is equivalent to $D$ and can be expressed as [41]

$$S_1 = x_1\mu_{12}\mu_{13} + x_2\mu_{12}\mu_{23} + x_3\mu_{23}\mu_{13} = 0 \quad (3.1)$$

where the shorthand notation $\mu_{ij} = \partial \mu_i / \partial n_j$ has been used.

To obtain the slope of the critical curve, we differentiate Eq. (3.1)

$$dS_1 = \left(\frac{\partial S_1}{\partial T}\right) dT + \left(\frac{\partial S_1}{\partial P}\right) dP + \left(\frac{\partial S_1}{\partial x_3}\right) dx_3 = 0 \quad (3.2)$$

Since the experiment was carried out under constant pressure, $dP = 0$, Eq. (3.2) gives the slope of the critical curve

$$\frac{dT}{dx_3} = -\frac{(\partial S_1/x_3)}{(\partial S_1/\partial T)} \quad (3.3)$$

The chemical potentials of components in a ternary regular solution are expressed as

$$\mu_1 = \mu_1^o + RT \ln x_1 + \xi_{12}x_2^2 + \xi_{13}x_3^2 + x_2x_3(\xi_{12} - \xi_{23} + \xi_{13}) \quad (3.4a)$$

$$\mu_2 = \mu_2^o + RT \ln x_2 + \xi_{12}x_1^2 + \xi_{23}x_3^2 + x_1x_3(\xi_{23} - \xi_{13} + \xi_{12}) \quad (3.4b)$$

$$\mu_3 = \mu_3^o + RT \ln x_3 + \xi_{13}x_1^2 + \xi_{23}x_2^2 + x_1x_2(\xi_{13} - \xi_{12} + \xi_{23}) \quad (3.4c)$$

We now can compute the differentials $\mu_{ij}$ in Eq. (3.1)
\[ \mu_{12} = \left( \frac{\partial \mu_1}{\partial n_2} \right)_{T,P,n_1,n_2} \]
\[ = -\frac{1}{n} \left[ RT - 2\xi_{12}x_2 + 2\xi_{12}x_2^2 + 2\xi_{13}x_3^2 + 2(\xi_{12} + \xi_{13} - \xi_{23})x_2x_3 - (\xi_{12} + \xi_{13} - \xi_{23})x_3 \right] \quad (3.5a) \]
\[ \mu_{13} = \left( \frac{\partial \mu_1}{\partial n_3} \right)_{T,P,n_1,n_2} \]
\[ = -\frac{1}{n} \left[ RT + 2\xi_{12}x_2^2 + 2(\xi_{12} + \xi_{13} - \xi_{23})x_2x_3 - (\xi_{12} + \xi_{13} - \xi_{23})x_2 + 2\xi_{13}x_3^2 - 2\xi_{13}x_3 \right] \quad (3.5b) \]
\[ \mu_{23} = \left( \frac{\partial \mu_2}{\partial n_3} \right)_{T,P,n_1,n_2} \]
\[ = -\frac{1}{n} \left[ RT + 2\xi_{12}x_1^2 + 2(\xi_{12} + \xi_{13} - \xi_{23})x_1x_3 - (\xi_{12} + \xi_{23} - \xi_{13})x_1 + 2\xi_{23}x_3^2 - 2\xi_{23}x_3 \right] \quad (3.5c) \]

As we discussed in the previous chapter, the critical point of component 1 and component 2 in a mixture is characterized by

\[ x_1 = x_2 = x_3 = 0.5; \quad T_c^0 = \frac{\bar{\xi}_{12}}{2R} \quad (3.6) \]

Substituting Eq. (3.6) and the condition \( x_3 = 0 \) into Eqs. (3.5), we have

\[
\begin{cases}
(\mu_{12})_c = 0 \\
(\mu_{13})_c = -\frac{1}{2n}(\xi_{12} + \xi_{23} - \xi_{13}) \\
(\mu_{23})_c = -\frac{1}{2n}(\xi_{12} + \xi_{13} - \xi_{23})
\end{cases}
\quad (3.7)
\]

With \( x_3 = 0 \), we now evaluate the partial derivative of \( S_1 \) at the critical point,
\[
\left( \frac{\partial S_1}{\partial T} \right)_c = x_1 \mu_{12} \frac{\partial \mu_{13}}{\partial T} + x_1 \mu_{13} + x_2 \mu_{12} \frac{\partial \mu_{23}}{\partial T} + x_2 \mu_{12} \frac{\partial \mu_{23}}{\partial T}
\]

(3.8)

and

\[
\left( \frac{\partial S_1}{\partial x_3} \right)_c = x_1 \mu_{12} \frac{\partial \mu_{13}}{\partial x_3} + x_1 \mu_{13} + x_2 \mu_{12} \frac{\partial \mu_{23}}{\partial x_3} + x_2 \mu_{12} \frac{\partial \mu_{23}}{\partial x_3} + \mu_{23} \mu_{13}
\]

(3.9)

Substituting Eqs (3.5) and Eqs (3.7) into the above equations, we have

\[
\left( \frac{\partial S_1}{\partial T} \right)_c = \frac{R}{4n^2} (\xi_{12} + \xi_{23} - \xi_{13}) + \frac{R}{4n^2} (\xi_{12} + \xi_{13} - \xi_{23}) = \frac{R \xi_{12}}{2n^2}
\]

(3.10)

\[
\left( \frac{\partial S_1}{\partial x_3} \right)_c = \frac{(\xi_{12} + \xi_{23} - \xi_{13})(\xi_{12} + \xi_{13} - \xi_{23})}{4n^2}
\]

(3.11)

Substituting Eq (3.10) and Eq (3.11) into Eq. (3.3), the dependence of the critical temperature on \(x_3\) is given by

\[
\left( \frac{dT}{dx_3} \right)_c = -\frac{1}{2R} \frac{(\xi_{12} + \xi_{23} - \xi_{13})(\xi_{12} + \xi_{13} - \xi_{23})}{\xi_{12}}
\]

(3.12)

Prigogine and Defray [41] state that when \(\xi_{12} \approx \xi_{23}\), the solubility of component 3 is about the same in both component 1 and 2. This leads to decrease in the critical temperature. By contrast, when component 3 is very much less soluble in one of the components than the other, e.g., \(\xi_{23} > \xi_{13}\) and \(\xi_{23} > \xi_{12}\), the critical temperature is increased.
3.2 The Supercritical Solubility in Multicomponent Systems

In the case of the dissolution of a chemically reactive solid in a binary mixture, a chemical reaction can be initiated. The Gibbs-Duhem equation for the system consisting of \( j \) components is expressed by

\[
\sum_{i=1}^{j} x_i d\mu_i = -\tilde{S}dT + \tilde{V}dP \tag{3.13}
\]

The sum of the mole fraction is

\[
\sum_{i=1}^{j} x_i = 1
\]

Substituting the above equation into Eq. (3.13), we obtain

\[
d\mu_j = -\tilde{S}dT + \tilde{V}dP - \sum_{i=1}^{j-1} x_i (d\mu_i - d\mu_j)
\]

If we let \( d\mu_{i,j} = d(\mu_i - \mu_j) = d\mu_i - d\mu_j \), then

\[
d\mu_j = -\tilde{S}dT + \tilde{V}dP - \sum_{i=1}^{j-1} x_i d\mu_{i,j}
\]

We choose the dependent potential to be

\[
f(T, P, \mu_{1,j}, \ldots) = \mu_j
\]

then

\[
\tilde{S} = -\left( \frac{\partial f}{\partial T} \right)_{P, \mu_{1,j}, \ldots}, \quad \tilde{V} = \left( \frac{\partial f}{\partial P} \right)_{T, \mu_{1,j}, \ldots}, \quad -x_i = \left( \frac{\partial f}{\partial \mu_{1,j}} \right)_{P,T, \ldots}
\]

are the conjugate densities.
Let component 1 be the solid dissolving in the system, with one density, $x_2$, held fixed. The derivative of mole fraction of component 1 with respect to temperature is given by

$$\left(\frac{\partial x_1}{\partial T}\right)_{x_2} = \frac{D(T, \mu_{2,j})}{D(\mu_{2,j})}$$

According to the Griffiths-Wheeler rule, the quantity

$$D(\mu_{2,j}) = \left(\frac{\partial x_2}{\partial \mu_{2,j}}\right)_{T,P}$$

will be strongly divergent at the critical point because its path makes an angle with the coexistence surface. The numerator

$$D(T, \mu_{2,j}) = \begin{bmatrix} \frac{\partial S}{\partial T} & \frac{\partial S}{\partial \mu_{2,j}} \\ \frac{\partial x_2}{\partial T} & \frac{\partial x_2}{\partial \mu_{2,j}} \\ \frac{\partial \mu_{2,j}}{\partial T} & \frac{\partial \mu_{2,j}}{\partial \mu_{2,j}} \end{bmatrix}$$

is expected to be strongly times weakly divergent as it possesses a vector that is not parallel to the coexistence surface, and a vector is parallel to the coexistence surface but not parallel to the critical surface. Hence, $(\partial x_1/\partial T)_{x_2}$ should diverge weakly at the critical surface. If there were two densities held fixed, the derivative

$$\left(\frac{\partial x_1}{\partial T}\right)_{x_2,x_3} = \frac{D(T, \mu_{3,j}, \mu_{2,j})}{D(\mu_{3,j}, \mu_{2,j})} \quad (3.14)$$

should not diverge at all.
The critical exponent of the derivative \( \partial x_1 / \partial T \) can be derived from the scaling hypothesis. Recall Eq. (2.53), the differential of the grand potential in the system with \( j \) components is expressed as

\[
d\phi_G = -SdT - \sum_{i=1}^{j} n_i d\mu_i
\]  

(3.15)

The grand potential \( \phi_G(t, \mu) \) is assumed to be a generalized homogeneous function at the critical point by the scaling hypothesis.

\[
\lambda \phi_G(t, \{\mu_i\}) = \phi_G(\lambda^a t, \{\lambda^a \mu_i\})
\]

(3.16)

where the variables are replaced by reduced variables

\[
t = \frac{|T - T_c|}{T_c}
\]

(3.17a)

\[
\mu_i = \frac{|\mu_i - \mu_c|}{\mu_c}
\]

(3.17b)

where \( \mu_i \) is the chemical potential of component \( i \), \( \mu_c \) is the chemical potential at the critical point.

The amount of component \( i \) can be derived from

\[
n_i = -\left( \frac{\partial \phi_G}{\partial \mu_i} \right)_T
\]

Taking first order of partial derivative on both sides of Eq. (3.16) with respect to \( \mu_i \), we get

\[
n_i(t, \{\mu_i\}) = \lambda^{a_i n_i^{-1}} n_i(\lambda^a t, \{\lambda^a \mu_i\})
\]

(3.18)

At the critical point, the above equation becomes
\[ n(0, \{0\}) = \lambda^{a_i-1} n(0, \{0\}) \]  

(3.19)

Subtracting Eq. (3.19) from Eq. (3.18)

\[ n_i(t, \{\mu_i\}) - n(0, \{0\}) = \lambda^{a_i-1} \left[ n_i(\lambda^{a_i} t, \{\lambda^{a_i} \mu_i\}) - n(0, \{0\}) \right] \]  

(3.20)

At equilibrium \( \nu = 0 \), the above equation becomes

\[ n_i(t, \{0\}) = \lambda^{a_i-1} \left[ n_i(\lambda^{a_i} t, 0) - n_i(0, \{0\}) \right] + n_i(0, \{0\}) \]  

(3.21)

The above equation must be held for all \( \lambda^{a_i} t \) including \( \lambda^{a_i} t = 1 \), so

\[ n_i(t, \{0\}) = t^{1-a_{\nu}} \left[ n_i(1,0) - n_i(0, \{0\}) \right] + n_i(0, \{0\}) \]  

(3.22)

Dividing both sides with the number of total moles, Eq. (3.22) becomes

\[ x_i(t, \{0\}) = t^{1-a_{\nu}} \left[ x_i(1,0) - x_i(0, \{0\}) \right] + x_i(0, \{0\}) \]  

(3.22)

Comparing Eq. (3.22) with Eq. (2.68) terms by terms, we get the critical exponent of the mole fraction of component \( i \) is \( \beta \),

\[ x_i \sim t^\beta \]

Hence, the partial derivative of the mole fraction with respect to temperature is

\[ \frac{\partial x_i}{\partial T} \sim t^{\beta - 1} \]

which agrees with the prediction of weak divergence.

Now we determine the direction of the divergence. We first write the stoichiometry of a general reaction
\[ v_1(1) + v_2(2) \rightarrow v_3(3) + v_4(4) \]  

(3.23)

where \(v_1, v_2, v_3\) and \(v_4\) are respective stoichiometric coefficients. The differential change of Gibbs free energy, \(G\), of the system can be described by the Gibbs equation

\[ dG = -SdT + VdP + \sum_{i} \mu_i d\eta_i \]  

(3.24)

Let \(d\eta_i = v_i d\eta\), where \(\eta\) is the extent of chemical reactions, \(v_i > 0\) refers to products and \(v_i < 0\) refers to reactants, we rewrite Eq. (3.24)

\[ dG = -SdT + VdP + \sum_{i} v_i \mu_i d\eta \]  

(3.25)

By applying the differential of \(\eta\) on both sides, we get

\[ \left( \frac{\partial G}{\partial \eta} \right)_{T,P} = \sum_{i} v_i \mu_i \]  

(3.26)

The difference of Gibbs free energy, \(\Delta G\), which maintains the separation of reactants and products

\[ \Delta G = v_3 \mu_3 + v_4 \mu_4 - v_1 \mu_1 - v_2 \mu_2 \]  

(3.27)

equals zero when \(\eta = \eta^e\), the equilibrium value of the extent of reaction.

Substituting Equation (3.26) into Equation (3.27), we get

\[ \left( \frac{\partial G}{\partial \eta} \right)_{T,P} = \Delta G \]  

(3.28)

Because \(\Delta G = 0\) when the system reaches equilibrium, \(G(\eta)\) takes on an extremum. For a stable equilibrium, the second derivative of \(G(\eta)\) must satisfy
\[
\left( \frac{\partial^2 G}{\partial \eta^2} \right)_{T,P} = \left( \frac{\partial \Delta G}{\partial \eta} \right)_{T,P} > 0 \tag{3.29}
\]

Since \( \Delta G \) depends on \( P, T, \) and \( \eta \), the differential of \( \Delta G / T \) can be written as

\[
d \left( \frac{\Delta G}{T} \right) = \left( \frac{\partial (\Delta G / T)}{\partial P} \right)_{\eta,T} dP + \left( \frac{\partial (\Delta G / T)}{\partial T} \right)_{\eta,P} dT + \left( \frac{\partial (\Delta G / T)}{\partial \eta} \right)_{T,P} d\eta \tag{3.30}
\]

When the system reaches equilibrium at constant pressure, the term on the left side and the first term on the right side equal zero. The above equation becomes

\[
\left( \frac{\partial \eta}{\partial T} \right)_{P} = -\frac{\left( \frac{\partial (\Delta G / T)}{\partial \eta} \right)_{\eta,P}}{\left( \frac{\partial (\Delta G / T)}{\partial T} \right)_{\eta,P}} \tag{3.31}
\]

Substituting the Gibbs-Helmholtz equation

\[
\left( \frac{\partial (\Delta G / T)}{\partial T} \right)_{\eta,P} = -\frac{\Delta H}{T^2} \tag{3.32}
\]

into Equation (3.31), we get

\[
\left( \frac{\partial \eta}{\partial T} \right)_{P} = \frac{\Delta H}{T} \left( \frac{\partial \eta}{\partial \Delta G} \right)_{T,P} \tag{3.33}
\]

where \( \Delta H \) is the dissolution enthalpy.

The derivative of reaction extent with respect to temperature, \( \partial \eta / \partial T \), is a derivative of density with respect to the field. With one density held fixed, it diverges weakly at the critical point.

Because the solubility, \( s \), in ppm is proportional to the extent of chemical reactions
\[ s = 10^6 \frac{M\eta}{m_{tot}} \]  \hspace{1cm} (3.34)

where \( M \) is the atomic weight of solute and \( m_{tot} \) is the total mass of solutions, substituting Eq. (3.34) into Eq. (3.33)

\[ \left( \frac{\partial \eta}{\partial T} \right)_p = \frac{\Delta H}{T} \left( \frac{\partial s}{\partial \Delta G} \right)_{T,p} \]  \hspace{1cm} (3.35)

We now rewrite the left side of Eq. (3.35) in the van’t Hoff form

\[ -\frac{s}{T^2} \left( \frac{\partial \ln s}{\partial (1/T)} \right)_p = s \frac{\Delta H}{T} \left( \frac{\partial \ln s}{\partial \Delta G} \right)_{T,p} \]  \hspace{1cm} (3.36)

\[ \left( \frac{\partial \ln s}{\partial (1/T)} \right)_p = -T\Delta H \left( \frac{\partial \ln s}{\partial \Delta G} \right)_{T,p} \]  \hspace{1cm} (3.37)

Since the equilibrium stability requires \( (\partial \Delta G / \partial \eta) > 0 \), i.e., \( (\partial \ln s / \partial \Delta G) > 0 \), in the critical region, \( (\partial \ln s / \partial \Delta G) \) goes to positive infinity, as the slope, \( (\partial \ln s / \partial (1/T)) \), goes to positive infinity in the exothermic dissolution reaction, \( \Delta H < 0 \), while the slope in the endothermic dissolution reaction, \( \Delta H < 0 \), goes to negative infinity.

### 3.3 The Critical Opalescence in Multicomponent Systems

The light scattering occurring at the critical point is the so-called critical opalescence. A. Einstein and M. Smoluchowski contributed the idea that, as the system approaches a critical point, there are fluctuations in relative permittivity (square of the reflective index). The fluctuations have their origin in fluctuations in the concentrations of the chemical components making up the
material. The concentration fluctuations can increase in size until they are of the same order of
magnetite as the wavelength of the incident light. [32,33] Since it was discovered by Cagniard de
la Tour in 1822, [5] the critical opalescence has been used to identify the critical points of pure
fluids and binary mixtures. We were able to associate the concentration fluctuations with certain
thermodynamic derivatives and develop a method to suppress the critical opalescence.

In the critical region, the incident light is scattered by the fluctuations in relative
permittivity the same way as the sunlight is scattered by the air molecules which causes the blue
sky. According to the Ornstein – Zernicke theory of light scattering, the turbidity, $\tau^*$, of a
homogeneous medium is

$$
\tau^* = \frac{8\pi^3 \nu}{3\lambda^4} \left\langle (\Delta \varepsilon_r)^2 \right\rangle
$$

(3.38)

where $\Delta \varepsilon_r$ is the fluctuation in relative permittivity, $\nu$ is the scattering volume, $\lambda$ is the incident
light wavelength. Since $\varepsilon_r$ is fluctuating at the critical point, we assume that $\varepsilon_r \sim \varepsilon_r(u)$ is a
function of fluctuations, $u$.

The Taylor series expansion of $\varepsilon_r(u)$ about $\langle \varepsilon_r \rangle$ is

$$
\varepsilon_r = \langle \varepsilon_r \rangle + \sum_k \left( \frac{\partial \varepsilon_r}{\partial u_k} \right)_{u_r} (u_k - \langle u_k \rangle)
$$

$$
\varepsilon_r - \langle \varepsilon_r \rangle = \sum_k \left( \frac{\partial \varepsilon_r}{\partial \varepsilon_r} \right)_{u_r} (u_k - \langle u_k \rangle)
$$

(3.39)
where \( u_r \) means all elements of \( u \) except the ones indicated in the differentiation. The variance of \( \varepsilon_r(u) \) is defined by

\[
\langle (\Delta \varepsilon_r)^2 \rangle = \langle (\varepsilon_r - \langle \varepsilon_r \rangle)^2 \rangle
\]

\[
\text{var} \left( \sum_k \left( \frac{\partial \varepsilon_r}{\partial u_k} \right)_{u_r} (u_k - \langle u_k \rangle) \right) = \text{cov} \left( \sum_k \left( \frac{\partial \varepsilon_r}{\partial u_k} \right)_{u_r} (u_k - \langle u_k \rangle), \sum_l \left( \frac{\partial \varepsilon_r}{\partial u_l} \right)_{u_r} (u_l - \langle u_l \rangle) \right)
\]

\[
= \sum_k \sum_l \left( \frac{\partial \varepsilon_r}{\partial u_k} \right)_{u_r} \left( \frac{\partial \varepsilon_r}{\partial u_l} \right)_{u_r} \text{cov} \left( (u_k - \langle u_k \rangle), (u_l - \langle u_l \rangle) \right)
\]

\[
= \sum_k \sum_l \left( \frac{\partial \varepsilon_r}{\partial u_k} \right)_{u_r} \left( \frac{\partial \varepsilon_r}{\partial u_l} \right)_{u_r} \langle \Delta u_k \Delta u_l \rangle
\]

Now we separate the variables into fixed variables, \( a \), and fluctuating variables, \( b \), then Eq. (3.40) becomes

\[
\langle (\Delta \varepsilon_r)^2 \rangle_a = \sum_k \sum_l \left( \frac{\partial \varepsilon_r}{\partial b_k} \right)_{a,b_r} \left( \frac{\partial \varepsilon_r}{\partial b_l} \right)_{a,b_r} \langle \Delta b_k \Delta b_l \rangle_a
\]

The covariance term \( \langle \Delta b_k \Delta b_l \rangle_a \) can be determined by setting up a grand canonical ensemble whose fixed variables are the temperature, \( T \), pressure, \( p \), and the amounts of each component \( n \) where \( n = \{ n_1, n_2, ..., n_q \} \).
Hence,

\[
\langle (\Delta \varepsilon_r)^2 \rangle = \sum_k \sum_l \left( \frac{\partial \varepsilon_r}{\partial n_k} \right)_{\{T,p,n_r\}} \left( \frac{\partial \varepsilon_r}{\partial n_l} \right)_{\{T,p,n_r\}} \langle \Delta n_k \Delta n_l \rangle_{\{T,p\}}
\]  \tag{3.42}

The partition function, \( Z \), for the grand canonical ensemble is

\[
Z = \int \cdots \int \exp \left[ \beta \sum_i^q (\mu_i n_i - E_i) \right] dn_1 \cdots dn_q
\]  \tag{3.43}

where \( \mu = \{\mu_1, \mu_2, \ldots, \mu_3\} \) are the collection of chemical potentials of each component in the ensemble, and \( \{E_i\} \) is the ensemble of energy states. The partial derivative of the partition function \( Z \) with respect to \( \mu_k \) is

\[
\frac{\partial Z}{\partial \mu_k} = \beta \cdot \int \cdots \int n_k \cdot \exp \left[ \beta \sum_i^q (\mu_i n_i - E_i) \right] dn_1 \cdots dn_q
\]  \tag{3.44}

The average of \( n_k \) is

\[
\langle n_k \rangle_{\{T,p\}} = \frac{1}{Z} \int \cdots \int n_k \cdot \exp \left[ \beta \sum_i^q (\mu_i n_i - E_i) \right] dn_1 \cdots dn_q
\]  \tag{3.45}

By differentiating Eq. (3.45) with respect to \( \mu_l \), we have

\[
\frac{1}{Z} \left( \frac{\partial}{\partial \mu_l} \int \cdots \int n_k \cdot \exp \left[ \beta \sum_i^q (\mu_i n_i - E_i) \right] dn_1 \cdots dn_q \right)_{\{T,p,n_r\}} - \langle n_k \rangle_{\{T,p\}} \frac{1}{Z} \frac{\partial Z}{\partial \mu_l} = \left( \frac{\partial \langle n_k \rangle}{\partial \mu_l} \right)_{\{T,p,n_r\}}
\]  \tag{3.46}

From Equation. (3.46), we get the covariance of \( \langle \Delta n_k \Delta n_l \rangle_{\{T,p\}} \)
\( (\Delta n_k \Delta n_l)_{\{T,p\}} = (n_k n_l)_{\{T,p\}} - \langle n_k \rangle_{\{T,p\}} \langle n_l \rangle_{\{T,p\}} = \frac{1}{\beta} \left( \frac{\partial \langle n_k \rangle}{\partial \mu_l} \right)_{\{T,p,\mu_r\}} \)  

(3.47)

Substituting Equation (3.47) into Equation (3.42), the variance of relative permittivity, \( \langle (\Delta \varepsilon_r)^2 \rangle \), can be determined by

\[
\langle (\Delta \varepsilon_r)^2 \rangle = \frac{1}{\beta} \sum_k \sum_l \left( \frac{\partial \varepsilon_r}{\partial n_k} \right)_{\{T,p,n_r\}} \left( \frac{\partial \varepsilon_r}{\partial n_l} \right)_{\{T,p,n_r\}} \left( \frac{\partial \langle n_k \rangle}{\partial \mu_l} \right)_{\{T,p,\mu_r\}}
\]  

(3.48)

Hence, by virtue of Eq. (3.38), the turbidity of mixtures can be cast in the form

\[
\tau^* = \frac{8\pi^3 v RT}{3\lambda^4} \sum_k \sum_l \left( \frac{\partial \varepsilon_r}{\partial n_k} \right)_{\{T,p,n_r\}} \left( \frac{\partial \varepsilon_r}{\partial n_l} \right)_{\{T,p,n_r\}} \left( \frac{\partial \langle n_k \rangle}{\partial \mu_l} \right)_{\{T,p,\mu_r\}}
\]  

(3.49)

We can change the subscripts into the same by replacing the last term with its reciprocal

\[
\tau^* = \frac{8\pi^3 v RT}{3\lambda^4} \sum_k \sum_l \left( \frac{\partial \varepsilon_r}{\partial n_k} \right)_{\{T,p,n_r\}} \left( \frac{\partial \varepsilon_r}{\partial n_l} \right)_{\{T,p,n_r\}} \left( \frac{\partial \mu_l}{\partial n_k} \right)_{\{T,p,n_r\}}^{-1}
\]  

(3.50)

Recall the Gibbs free energy of mixing for the binary regular solution in Eq. (2.39)

\[
\Delta \tilde{G}_{mix} = RT(x_1 \ln x_1 + x_2 \ln x_2) + \xi x_1 x_2
\]  

(3.51)

The critical condition of regular binary mixtures at constant pressure is

\[
x_c = x_1 = x_2 = \frac{1}{2} \quad \xi = 2RT_c
\]  

(3.52)
The chemical potential, $\mu_i$, for component $i$ is

$$\begin{align*}
\mu_1 &= \mu_1^0 + RT \ln x_1 + \xi x_2^2 \\
\mu_2 &= \mu_2^0 + RT \ln x_2 + \xi x_1^2 \\
\end{align*}$$

(3.53)

After differentiating Eqs. (3.53), and substituting Eq. (3.52), the derivatives of the chemical potentials are

$$\left( \frac{\partial \mu_1}{\partial n_1} \right)_{T=\bar{T}_c} = 0; \quad \left( \frac{\partial \mu_2}{\partial n_2} \right)_{T=\bar{T}_c} = 0; \quad \left( \frac{\partial \mu_1}{\partial n_2} \right)_{T=\bar{T}_c} = 0$$

Hence, at the critical point,

$$\left( \frac{\partial \mu_1}{\partial n_1} \right)^{-1}_{T_c,p,x_c} = \infty; \quad \left( \frac{\partial \mu_2}{\partial n_2} \right)^{-1}_{T_c,p,x_c} = \infty; \quad \left( \frac{\partial \mu_1}{\partial n_2} \right)^{-1}_{T_c,p,x_c} = \infty$$

(3.54)

For a binary system with component 1, which is treated as the solvent, and component 2, which is treated as the solute, hence $n_2$ is fluctuating at the critical point. The fixed variables set $a = \{T, p, n_1\}$ and fluctuated variable set $b = \{n_2\}$ in Eq. (3.50).

$$\tau^* = \frac{8\pi^3 v RT}{3\lambda^4 N_A} \left[ \left( \frac{\partial \varepsilon_r}{\partial n_2} \right)_{T,p,n_2} \left( \frac{\partial \mu_1}{\partial n_1} \right)^{-1}_{T,p,n_2} + \left( \frac{\partial \varepsilon_r}{\partial n_1} \right)_{T,p,n_1} \left( \frac{\partial \mu_2}{\partial n_2} \right)^{-1}_{T,p,n_2} \right]
+ 2 \left( \frac{\partial \varepsilon_r}{\partial n_1} \right)_{T,p,n_2} \left( \frac{\partial \varepsilon_r}{\partial n_2} \right)_{T,p,n_1} \left( \frac{\partial \mu_1}{\partial n_2} \right)^{-1}_{T,p,n_1}$$

(3.55)

As a result,
Again, let \( \tau^* \) point.

It is still difficult to evaluate the differentials of chemical potential \( \mu \), hence the turbidity diverges toward infinity at the critical point.

For a ternary mixture, the turbidity in Eq. (3.50) is expressed as

\[
\tau^* = \frac{8\pi^3 \nu RT}{3\lambda^4 N_A} \left[ \left( \frac{\partial \varepsilon_r^2}{\partial n_1^2} \right)_{(T,p,n_r)} \left( \frac{\partial \mu_1}{\partial n_1} \right)_{(T,p,n_r)}^{-1} + 2 \left( \frac{\partial \varepsilon_r}{\partial n_1} \right)_{(T,p,n_r)} \left( \frac{\partial \varepsilon_r}{\partial n_2} \right)_{(T,p,n_r)} \left( \frac{\partial \mu_1}{\partial n_2} \right)_{(T,p,n_r)}^{-1} \right. \\
\left. + \left( \frac{\partial \varepsilon_r^2}{\partial n_2^2} \right)_{(T,p,n_r)} \left( \frac{\partial \mu_2}{\partial n_2} \right)_{(T,p,n_r)}^{-1} + 2 \left( \frac{\partial \varepsilon_r}{\partial n_2} \right)_{(T,p,n_r)} \left( \frac{\partial \varepsilon_r}{\partial n_3} \right)_{(T,p,n_r)} \left( \frac{\partial \mu_2}{\partial n_3} \right)_{(T,p,n_r)}^{-1} \right]
\]

(3.57)

Although the ratio of component 1 and component 2 is fixed during the experiment and the chemical potential of each component for the ternary regular mixture is given by,

\[
\mu_1 = \mu_1^0 + RT[\ln x_1 + \xi_{12}x_2^2 + \xi_{13}x_3^2 + (\xi_{12} + \xi_{13} - \xi_{23})x_2x_3] \\
\mu_2 = \mu_2^0 + RT[\ln x_2 + \xi_{12}x_1^2 + \xi_{23}x_3^2 + (\xi_{12} + \xi_{23} - \xi_{13})x_1x_3] \\
\mu_3 = \mu_3^0 + RT[\ln x_3 + \xi_{13}x_1^2 + \xi_{23}x_2^2 + (\xi_{13} + \xi_{23} - \xi_{12})x_1x_2]
\]

(3.58)

It is still difficult to evaluate the differentials of chemical potentials in Eq. (3.50) at the critical point.

However, the critical exponent of turbidity can be derived from the scaling hypothesis.

Taking second order of partial derivative on both sides of Eq. (3.16) with respect to \( \mu_i \), we get

\[
\frac{\partial n_i(t, \{\mu_i\})}{\partial \mu_i} = \lambda^{2a_{\mu_i} - 1} \frac{\partial n_i(\lambda^{a_{\mu_i}} t, \{\lambda^{a_{\mu_i}} \mu_i\})}{\partial \mu_i}
\]

(3.59)

Again, let \( \lambda^{a_{\mu_i}} t = 1 \) for the above equation,

67
\[
\frac{\partial n_i(t, \{\mu_i\})}{\partial \mu_i} = t^{1-2a_{\mu_i}} \frac{\partial n_i(1, \{\lambda^a_{\mu_i} \mu_i\})}{\partial \mu_i}
\]

At the critical equilibrium \(\{\mu_i\} = 0\), the above partial derivative is

\[
\frac{\partial n_i(t, \{\mu_i\})}{\partial \mu_i} = t^{1-2a_{\mu_i}} \frac{\partial n_i(1, \{0\})}{\partial \mu_i}
\]

\[
\frac{\partial n_i(t, \{\mu_i\})}{\partial \mu_i} \frac{\partial \mu_i}{\partial \mu_i} = t^{1-2a_{\mu_i}} \frac{\partial n_i(1, \{0\})}{\partial \mu_i} \frac{\partial \mu_i}{\partial \mu_i}
\]

\[
\frac{\partial n_i(t, \{\mu_i\})}{\partial \mu_i} = t^{1-2a_{\mu_i}} \frac{\partial n_i(1, \{0\})}{\partial \mu_i}
\] (3.60)

Comparing Eq. (3.60) with Eq. (2.72), one can find that the critical exponent of the partial derivatives in Eq. (3.57) is

\[
\frac{\partial n_i(t, \{\mu_i\})}{\partial \mu_i} \sim t^{-\gamma}
\]

Therefore,

\[
\tau^* \sim t^{-\gamma}
\] (3.61)

Like solubility, the existence of the divergence of turbidity is determined by the number of fixed densities. To predict the existence of the divergence, we first convert the partial derivatives of chemical potentials in Eq. (3.57) to intensive variables.

\[
\left( \frac{\partial \mu_i}{\partial n_i} \right)^{-1} = \frac{\partial n_i}{\partial x_i} \frac{\partial x_i}{\partial \mu_i} = \frac{n}{1-x_i} \frac{\partial x_i}{\partial \mu_i}
\]

\[
\left( \frac{\partial \mu_i}{\partial n_j} \right)^{-1} = \frac{\partial n_j}{\partial x_i} \frac{\partial x_i}{\partial \mu_i} = -\frac{n}{x_i} \frac{\partial x_i}{\partial \mu_i}
\]
Because the mole fraction has a unique value and the chemical potential is uniform in each coexisting phase, the derivative \( \frac{\partial x_i}{\partial \mu_i} \) is the derivative of a density with respect to a field.

According to the phase rule, if there were two coexisting phases, the number of independent variables in the ternary system is

\[
F = C - P + 2 = 3 - 2 + 2 = 3
\]

(3.62)

Since the intensive variables, \( T \), and \( P \), are fixed by the experimental conditions, \( F = 3 \) implies that only one mole fraction is fixed. As a result, the derivatives \( \frac{\partial x_i}{\partial \mu_i} \) will diverge toward infinity as \( T \to T_c \). In contrast, if there was only one homogenous phase, the number of independent variables becomes

\[
F = C - P + 2 = 3 - 1 + 2 = 4
\]

(3.63)

According to the Griffiths-Wheeler rule, the derivatives \( \frac{\partial x_i}{\partial \mu_i} \) should remain finite in the critical region because there are two fixed densities, and the critical opalescence is not to be expected.

Hence, we predict that the addition of a sufficiently soluble solute to a binary liquid mixture should be sufficient to quench the opalescence.
CHAPTER 4 THE DISSOLUTION IN MULTICOMPONENT SYSTEMS AT THE CRITICAL POINT

In this chapter, we will use the phase rule and isomorphism principal analysis to predict the critical effect on solubilities in multicomponent systems. The phase rule is used to count the number of independent variables of each system. The critical properties will depend solely upon the number of independent variables, which will be otherwise independent of the chemical details. We expect to observe the critical effect for systems with less than four independent variables, \( F < 4 \), and no critical effect for the system with four independent variables, \( F = 4 \).

4.1 Experimental Materials

The liquid mixture systems examined for supercritical solubility are listed in Table. 4. System (1) was used to determine the critical effect in solubility behavior of a simple system without the chemical reaction occurring. The chemical reaction was introduced in systems (2)-(9). And the system complexity was increased by making two solutes dissolve simultaneously in reactions (6)-(9). In reactions (6) and (8),
Table 4. The reaction mixtures, sample preparations, and measurements for solubility experiments

<table>
<thead>
<tr>
<th>No</th>
<th>Solute</th>
<th>Solvent</th>
<th>$T_c^0/°C$</th>
<th>$T_c/°C$</th>
<th>Solute Amount (g)</th>
<th>Dilution Solvent</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>phenolphthalein</td>
<td>Nitrobenzene/Dodecane</td>
<td>28.12 ± 0.01</td>
<td>28.20 ± 0.01</td>
<td>1.20</td>
<td>$10^{-4}M NaOH$ solution</td>
<td>UV-Vis spectroscopy</td>
</tr>
<tr>
<td>2</td>
<td>BaCrO$_4$</td>
<td>IBA/Water</td>
<td>26.09 ± 0.01</td>
<td>25.92 ± 0.01</td>
<td>1.07</td>
<td>10% $HNO_3$ solution</td>
<td>ICP-ES</td>
</tr>
<tr>
<td>3</td>
<td>Ga$_2$O$_3$</td>
<td>IBA/Water</td>
<td>26.83 ± 0.01</td>
<td>26.85 ± 0.01</td>
<td>0.13</td>
<td>10% $HNO_3$ solution</td>
<td>ICP-ES</td>
</tr>
<tr>
<td>4</td>
<td>zinc (-)-tartrate</td>
<td>IBA/Water</td>
<td>26.49 ± 0.01</td>
<td>26.32 ± 0.01</td>
<td>0.51</td>
<td>10% $HNO_3$ solution</td>
<td>ICP-ES</td>
</tr>
<tr>
<td>5</td>
<td>glutamic (+)-acid</td>
<td>DGME/Water</td>
<td>10.93 ± 0.01</td>
<td>9.71 ± 0.01</td>
<td>2.01</td>
<td>distilled water</td>
<td>pH meter</td>
</tr>
<tr>
<td>6</td>
<td>Pbl$_2$/Na$_2$SO$_4$</td>
<td>IBA/Water</td>
<td>26.20 ± 0.01</td>
<td>26.66 ± 0.01</td>
<td>1.52/0.15</td>
<td>10% $HNO_3$ solution</td>
<td>ICP-ES</td>
</tr>
<tr>
<td>7</td>
<td>PbI$_2$/PbSO$_4$</td>
<td>IBA/Water</td>
<td>26.60 ± 0.01</td>
<td>26.68 ± 0.01</td>
<td>0.98/1.06</td>
<td>10% $HNO_3$ solution</td>
<td>ICP-ES</td>
</tr>
<tr>
<td>8</td>
<td>BaSO$_4$/CaSO$_4$</td>
<td>IBA/Water</td>
<td>27.12 ± 0.01</td>
<td>27.70 ± 0.01</td>
<td>2.52/2.59</td>
<td>10% $HNO_3$ solution</td>
<td>ICP-ES</td>
</tr>
<tr>
<td>9</td>
<td>zinc (+)-tartrate /zinc (-)-tartrate</td>
<td>IBA/Water</td>
<td>26.56 ± 0.01</td>
<td>26.13 ± 0.01</td>
<td>0.27/0.26</td>
<td>10% $HNO_3$ solution</td>
<td>ICP-ES</td>
</tr>
</tbody>
</table>
the predictive power of the phase rule was tested in a $F = 4$ case in which the critical effect is not expected. The reaction mixture (5) was used to investigate the critical effect on solubility behavior in the binary mixture with a lower solution critical temperature. Unlike the case of a solute dissolving in IBA + water, where the solvent component (IBA) is acidic, in reaction (5) where glutamic (+)-acid is dissolving in DGME + water, it is the solute component (glutamic (+)-acid) which is acidic. The reaction mixture (9) was used to observe the strong critical effect on solubility which is predicted in the $F = 2$ case. All the chemicals are used as received and water is distilled once from a glass system.

![Figure 11. Phase diagram of DGME + water mixture. [42]](image)

The nitrobenzene + dodecane and IBA + water mixtures have the upper critical solution temperatures (UCST). The critical point for nitrobenzene + dodecane mixture occurs at about 301 $K$ under atmospheric pressure and at the composition of 55.2% mass fraction of nitrobenzene. The critical point for IBA + water mixture occurs at about 299 $K$ under atmospheric pressure and the composition of 38.8% mass fraction of IBA, as shown in Fig. 2. The experiments involving nitrobenzene + dodecane and IBA +
water mixtures were carried out in the Chemical Physics Research Laboratory at the University of Alabama in Huntsville. The DGME + water mixture has a lower critical solution temperature (LCST), see Fig. 11. The critical point for DGME + water mixture occurs at about 284 $K$ under atmospheric pressure and at the composition of 13.0% mass fraction of DGME. The reaction in the DGME + water mixture was determined in the Structural Biology Laboratory at the University of Alabama in Huntsville. We chose to use those binary mixtures because their critical points are in the experimentally convenient range and the coexistence curves are flat in the critical region.

4.2 Experimental Methods

All experiments in this chapter were carried out along the critical isopleth, $x = x_c^0$. The binary mixtures were prepared by weighting with a precision of $\pm 5$ mg. In order to control and stabilize the system temperature, the mixtures and a magnetic stir bar were placed in a well-stoppered, Pyrex glass, flat bottom test tube with a 3 cm inside diameter. The test tube was held at the desired temperature by immersing it in a water bath in which the temperature could be controlled within 0.1$^\circ$C, as shown in Fig. 12. The temperature is controlled by an electric immersion heater operating in conjunction with a mercury thermoregulator. The temperature of the water bath could be measured with a digital platinum resistance thermometer with a reported accuracy of $\pm 0.001^\circ$C.
Once the sample test tube was put into the water bath, the critical temperature of the binary mixture was determined by the visual detection of critical opalescence and the disappearance of the meniscus. Fig. 13 describes the procedure used to find the critical temperature. Once the critical temperature was located, a solute was added in an amount sufficient to establish a coexisting solid phase. Since the dissolved solute shifts the critical temperature, the system temperature needed to be adjusted to find the new critical temperature.

In these solubility experiments, once the critical temperature was located, a small amount of aliquot was collected from the binary mixture by an adjustable pipet. Then it was diluted with an extra solvent to prevent precipitation at room temperature. The amount collected, the dilution ratio, and the extra solvent may vary depending on the kinds of solute and solvents used in the experiment.
Figure 13. The experimental procedure for the critical point determination
The diluted sample was stored in a 50 mL test tube covered with a cap to prevent the evaporation of the liquid. The thermostat temperature was adjusted to the next value, e.g., higher for systems with UCST or lower for systems with LCST, and the process of stirring followed by sedimentation was repeated. The samples were collected and processed the same way as the first sample. Because the value of solubility changes dramatically near the critical temperature, the temperature difference between samples collected in the critical region should be the smallest number as the condition allowed. Since it is a weak divergence in \( \ln s/(1/T) \) which is expected, the critical region was found at \( |T - T_c| \sim 0.8 \degree C \) in those experiments. Several samples were also collected outside the critical region to compare it with the critical behavior.

Due to the different nature of the solutes and solvents, several different methods and instruments were used to measure the concentrations of samples from each experiment. In the phenolphthalein experiment, each aliquot was mixed with 20 mL \( 10^{-4} M \) sodium hydroxide in a separation funnel. The phenolphthalein in the nitrobenzene + dodecane mixture was extracted by the sodium hydroxide solution that dyed the solution pink, so the concentration of phenolphthalein can be measured by UV-Vis spectroscopy. The concentration of phenolphthalein in each aliquot was determined with a GENESYS 10S UV-vis spectrophotometer set at the wavelength \( \lambda_{max} = 550 nm \). The spectrometer had been preciously calibrated with standard solutions of sodium hydroxide and phenolphthalein. One shall note that the time between the extraction and measurement for each sample needs to be the same to eliminate the effect of photodegradation. The dilute solution for the experiments involving metal salts is 10% \( HNO_3 \) solution so the samples can be homogenous solutions and the possible crystallization of the solutes is prevented. Because of the low solubility of the selected metal salts in the binary mixture, the concentration was measured by Inductively Coupled Plasma Emission Spectroscopy (ICP-ES). Some of the samples were diluted twice before analysis with 10% \( HNO_3 \) to keep the concentrations of IBA below the range of
the instrument. The concentration of metal ions in each aliquot was determined by ThermoScientific ICAP 6500 ICP-OES instrument, at the Advanced Materials Institute at Western Kentucky University. The instrument had been previously calibrated with standard solutions of corresponding metals. In the experiment on glutamic (+)-acid, each aliquot was diluted with 10 mL of distilled water because of the high solubility of glutamic (+)-acid and DGME in water at room temperature. Since the pH value of each aliquot depends on the concentration of glutamic acid, the amount of dissolved glutamic (+)-acid can be determined by the pH measurement. We analyzed the glutamic (+)-acid amount of the diluted aliquot by using an Orion™ Versa Star pH/conductivity Meter. The pH meter also had been previously calibrated with standard solutions of glutamic (+)-acid.

Table. 4 summarizes the reaction mixtures, sample preparations, and measurements for solubility experiments. The solute used in each solubility experiment is listed in column two of the Table. 4. Columns four and five show the original critical temperature, $T_C^0$ of the binary mixture and the critical temperature, $T_C$ after solutes added, respectively. The amount of solutes added in the binary mixture is listed in column six, while the dilution solvent for the aliquot is indicated in column seven. The last column shows the measurement method used.

### 4.3 The Dissolution of Phenolphthalein in Nitrobenzene + Dodecane

Because the phenolphthalein and the nitrobenzene + dodecane are chemically inert with respect to each other, there is no chemical reaction occurring in the dissolution. The system is similar to the metal alloy, hence, the number of independent variables in this system can be determined by the Gibbs phase rule in its original forms.

$$F = C - P + 2$$  \hspace{1cm} (4.1)
There are three components in the systems, so $C = 3$. During the experiment, there is a solid phase and a homogeneous liquid phase, so $P = 2$. According to Eq. (4.1), the number of independent variables is thus $F = 3$. Two of these are temperature and pressure, which are fields, the remaining variable is the ratio of the mole fractions of the two solvent components, which is a density. Hence, the derivative of a density with respect to a field, $(\partial \ln s / \partial (1/T))$, diverges at the critical point, i.e., the critical effect on the solubility of the phenolphthalein was predicted. The measurements of the concentration of phenolphthalein, $s$, as a function of temperature are plotted in van’t Hoff form with $\ln s$ vs. $1/T$ in Fig. 14. One can easily observe the divergence of the van’t Hoff slope, $(\partial \ln s / \partial (1/T))$, in the critical region.
Figure 14. Van’t Hoff plot of the temperature dependence of the solubility of phenolphthalein in nitrobenzene + dodecane mixture.
4.4 The Dissolution of Barium Chromate in IBA + Water

The reaction scheme of the dissolution of $BaCrO_4$ is

$$BaCrO_4(s) \rightarrow Ba^{2+}(aq) + CrO_4^{2-}(aq) \quad (4.2a)$$

$$H_3O^+(aq) + CrO_4^{2-}(aq) \rightarrow HCrO_4^-(aq) + H_2O \quad (4.2b)$$

$$HA(aq) + H_2O \rightarrow H_3O^+(aq) + A^-(aq) \quad (4.2c)$$

According to Eqs. (4.2), the components are: $H_2O, HA, H_3O^+, A^-, Ba^{2+}, CrO_4^{2-}, BaCrO_4,$ and $HCrO_4^-$, where $HA$ represents isobutyric acid and $A^-$ represents the isobutyrate ion. Counting these components, we see that

$$C = 8 \quad (4.3)$$

Five elements, $H, A, O, Ba,$ and $Cr$, are involved, which $A$ is a pseudo element because its internal covalent bonds are not disturbed in the reaction, hence $E = 5$.

The maximum number of linearly independent reactions connecting nine components spanned by five elements is

$$R = C - E = 8 - 5 = 3 \quad (4.4)$$

which agrees with the proposed reaction scheme.

Because of the addition of an excess of $BaCrO_4$ to the mixture, there are two phases, the liquid aqueous phase and the solid $BaCrO_4$, at chemical equilibriums, so

$$P = 2 \quad (4.5)$$

The invariant constraints of the system can be derived from the atomic conservation matrix.
Using elementary row operations,

\[
\begin{array}{cccccccc}
\text{Row} & H_2O & HA & BaCrO_4 & H_3O^+ & A^- & Ba^{2+} & CrO_4^{2-} & HCrO_4^- \\
H & 2 & 1 & 0 & 3 & 0 & 0 & 0 & 1 \\
A & 0 & 1 & 0 & 0 & 1 & 0 & 0 & 0 \\
O & 1 & 0 & 4 & 1 & 0 & 0 & 4 & 4 \\
Ba & 0 & 0 & 1 & 0 & 0 & 1 & 0 & 0 \\
Cr & 0 & 0 & 1 & 0 & 0 & 0 & 1 & 1 \\
\end{array}
\]

the rows without the reactants \( H_2O \), \( HA \), and \( BaCrO_4 \) give the invariant constraints that are both independent of the extent of reaction and independent of the initial conditions,

\[
0 = 2x_{Ba^{2+}} + x_{H_3O^+} - x_{HCrO_4^-} - 2x_{CrO_4^{2-}} - x_{A^-} \quad (4.6a)
\]

\[
0 = x_{Ba^{2+}} - x_{CrO_4^{2-}} - x_{HCrO_4^-} \quad (4.6b)
\]

where \( x_i \) is the mole fraction of component \( i \). Eqs. (4.6a) and (4.7b) express charge neutrality and mass conservation of barium, respectively. Thus, the number of invariant constraints in the system is given by

\[
I = 2 \quad (4.7)
\]

Evaluation of the generalized phase rule given in Eq. (2.85), we obtain

\[
F = C - P - R - I + 2 = 8 - 2 - 3 - 2 + 2 = 3
\]

In the case of the dissolution of \( BaCrO_4 \) in \( IBA + \) water, because the temperature, pressure, and one mole fraction are fixed, the critical point isomorphism principle predicts the divergence in \((\partial \ln s / \partial (1/T))\) as \( T \to T_c \). The measurements of barium solubility, \( s \), are plotted in van’t Hoff form with
\( \ln s \text{ vs. } 1/T \) in Fig. 15. It is clear from the figure that the van’t Hoff slope, \( (\partial \ln s/\partial (1/T)) \) diverges to positive infinity in the critical region.

Figure 15. Van’t Hoff plot of the temperature dependence of the solubility of barium in IBA + water
4.5 The Dissolution of Gallium (III) Oxide in IBA + Water

The dissolution of gallium oxide is original work by this author in collaboration with Rosa Mauro and was performed as a test of the predictive power of the phase rule. The reaction scheme of the dissolution of $Ga_2O_3$ is

$$Ga_2O_3(s) \rightarrow 2Ga^{3+}(aq) + 3O^{2-}(aq)$$

$$HA(aq) + H_2O \rightarrow H_3O^+(aq) + A^-(aq)$$

$$2H_3O^+(aq) + O^{2-}(aq) \rightarrow 3H_2O$$

(4.8)

Counting these components, $H_2O$, $HA$, $H_3O^+$, $A^-$,$Ga^{3+}$, $O^{2-}$ and $Ga_2O_3$, in Eq. (4.8), we obtain

$$C = 7$$

(4.9)

Four elements, $H$, $A$, $O$, and $Ga$, are involved, hence $E = 4$.

The maximum number of linearly independent reactions connecting seven components spanned by four elements is

$$R = C - E = 7 - 4 = 3$$

(4.10)

which agrees with the proposed reaction scheme.

Because of the addition of an excess of $Ga_2O_3$ to the mixture, there are two phases, the liquid aqueous phase and solid $Ga_2O_3$, at chemical equilibriums, so

$$P = 2$$

(4.11)

The invariant constraints of the system can be derived from the atomic conservation matrix.

<table>
<thead>
<tr>
<th></th>
<th>$H_2O$</th>
<th>$HA$</th>
<th>$Ga_2O_3$</th>
<th>$H_3O^+$</th>
<th>$A^-$</th>
<th>$Ga^{3+}$</th>
<th>$O^{2-}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H$</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>3</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$A$</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$O$</td>
<td>1</td>
<td>0</td>
<td>3</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>$Ga$</td>
<td>0</td>
<td>0</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
</tr>
</tbody>
</table>
Using elementary row operations,

<table>
<thead>
<tr>
<th></th>
<th>$H_2O$</th>
<th>$HA$</th>
<th>$Ga_2O_3$</th>
<th>$H_3O^+$</th>
<th>$A^-$</th>
<th>$Ga^{3+}$</th>
<th>$O^{2-}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H$</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>$\frac{9}{2}$</td>
<td>3</td>
</tr>
<tr>
<td>$A$</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$O$</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>$\frac{1}{2}$</td>
<td>0</td>
</tr>
<tr>
<td>$Ga$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>$-1$</td>
<td>3</td>
<td>$-2$</td>
</tr>
</tbody>
</table>

the last row without the reactants $H_2O$, $HA$ and $Ga_2O_3$ give the invariant constraint that is independent of the extent of reaction and independent of the initial conditions,

$$0 = 3x_{Ga^{3+}} + x_{H_3O^+} - 2x_{O^{2-}} - x_{A^-} \tag{4.12}$$

where $x_i$ is the mole fraction of component $i$. Eq. (4.12) expresses charge neutrality in the liquid phase.

Thus, the number of invariant constraints in the system is given by

$$I = 1 \tag{4.13}$$

Evaluation of the generalized phase rule given in Eq. (2.85), we obtain

$$F = C - P - R - I + 2 = 7 - 2 - 3 - 1 + 2 = 3$$

In the case of the dissolution of $Ga_2O_3$ in $IBA + water$, because the temperature, pressure, and one mole fraction are fixed, the critical point isomorphism principle predicts the divergence in $(\partial \ln s/\partial (1/T))$ as $T \rightarrow T_c$. The measurements of gallium solubility, $s$, are plotted in van’t Hoff form with $\ln s$ vs. $1/T$ in Fig. 16. It is clear from the figure that the van’t Hoff slope, $(\partial \ln s/\partial (1/T))$ diverges to negative infinity in the critical region.
Figure 16. Van’t Hoff plot of the temperature dependence of the solubility of gallium in IBA + water
4.6  The Dissolution of Zinc (-)-Tartrate in IBA + Water

Despite the dissolution of zinc (-)-tartrate in IBA + water may involve numerous intricate chemical processes because the critical effect solely depends on the number of fixed thermodynamic variables, the simplified reaction scheme is proposed as

\[
HA(aq) + H_2O \rightarrow H_3O^+(aq) + A^-(aq)
\]
\[
ZnT(s) \rightarrow Zn^{2+}(aq) + T^{2-}(aq)
\]

There are seven components, including \(H_2O, HA, H_3O^+, A^-, Zn^{2+}, T^{2-}\), and \(ZnT\), where \(T\) represents the tartrate anion. Hence,

\[
C = 7
\]  \(\text{(4.14)}\)

Five elements, \(H, A, O, Zn,\) and \(T\), are involved, which \(A\) and \(T\) are pseudo elements because their internal covalent bonds are not disturbed in the reaction, hence \(E = 5\).

The maximum number of linearly independent reactions connecting seven components spanned by five elements is

\[
R = C - E = 7 - 5 = 2
\]  \(\text{(4.15)}\)

which agrees with the proposed reaction scheme.

At equilibrium, the liquid aqueous phase and solid zinc (-) tartrate coexist in the reaction tube. Thus, the number of phases is

\[
P = 2
\]  \(\text{(4.16)}\)

We now construct the atomic conservation matrix.

\[
\begin{array}{cccccccc}
|   & H_2O & HA & ZnT & H_3O^+ & A^- & Zn^{2+} & T^{2-} \\
H  & 2    & 1  & 0   & 3       & 0   & 0       & 0       \\
A  & 0    & 1  & 0   & 0       & 1   & 0       & 0       \\
O  & 1    & 0  & 0   & 1       & 0   & 0       & 0       \\
Zn & 0    & 0  & 1   & 0       & 0   & 1       & 0       \\
T  & 0    & 0  & 1   & 0       & 0   & 0       & 1
\end{array}
\]
Using elementary row operations,

\[
\begin{array}{cccccccc}
 & H_2O & HA & ZnT & H_2O^+ & A^- & Zn^{2+} & T^{2-} \\
H & 1 & 0 & 0 & 0 & 1 & 0 & 0 \\
A & 0 & 1 & 0 & 0 & 1 & 0 & 0 \\
O & 0 & 0 & 1 & 0 & 0 & 0 & 1 \\
Zn & 0 & 0 & 0 & 1 & -1 & 2 & -2 \\
T & 0 & 0 & 0 & 0 & 0 & 1 & -1 \\
\end{array}
\]

the last two rows without the reactants \(H_2O\), \(HA\), and \(ZnT\) give invariant constraints that are both independent of the extent of reaction and independent of the initial conditions,

\[
0 = 2x_{Zn^{2+}} + x_{H_3O^+} - 2x_{T^{2-}} - x_{A^-} \quad (4.17a)
\]

\[
0 = x_{Zn^{2+}} - x_{T^{2-}} \quad (4.17b)
\]

where \(x_i\) is the mole fraction of component \(i\). Eqs. (4.17) express charge neutrality and mass conservation of zinc respectively. Thus, the number of invariant constraints in the system is given by

\[
I = 2 \quad (4.18)
\]

Evaluation of the generalized phase rule given in Eq. (2.85), we obtain

\[
F = C - P - R - I + 2 = 7 - 2 - 2 - 2 + 2 = 3
\]

In the case of the dissolution of \(ZnT\) in \(IBA + water\), because the temperature, pressure, and one mole fraction are fixed, the critical point isomorphism principle predicts the divergence in \((\partial \ln s / \partial (1/T))\) as \(T \to T_c\). The measurements of zinc solubility, \(s\), are plotted in van’t Hoff form with \(\ln s \ vs. 1/T\) in Fig. 17. It is clear from the figure that the van’t Hoff slope, \((\partial \ln s / \partial (1/T))\) diverges to positive infinity in the critical region.
Figure 17. Van’t Hoff plot of the temperature dependence of the solubility of zinc in IBA + water
4.7 The Dissolution of Glutamic (-)-Acid in DGME + Water

The Dissolution of Glutamic (-)-Acid in DGME + Water was performed as a test of the predictive power of the isomorphism principle and the phase rule when the acid/base role between the solvent and solute is switched. The chemical structures of glutamic (-)-acid, as shown in Fig. 18, shows that the carbon atom in the glutamic acid adjacent to the amino group is chiral.

![Chemical structures of glutamic (-)-acid](image)

Figure 18. Chemical structures of glutamic (-)-acid

When glutamic acid is dissolved in water, it becomes a zwitterion because of an internal transfer of a hydrogen ion from the carboxyl group to the amino group to leave an ion with both a negative charge and a positive charge, as shown below.

![Zwitterion structure](image)

The zwitterion interacts with water molecules acting as an acid. And the oxygen atom in the hydroxy group of DGME is a base and reacts with an acid by proton transfer to form an oxonium ion. [43]

\[
HG(s) + H_2O \rightarrow H_3O^+(aq) + G^-(aq)
\]

\[
ROH(aq) + H_2O^+ \rightarrow RH_2O^+(aq) + H_2O
\]
Based on the above reactions, there are 6 chemical species in the system, including $H_2O, HG, H_3O^+, G^-, ROH,$ and $RH_2O^+$, where $HG$ and $ROH$ represent the glutamic acid and $ROH$, respectively. Counting these components, we see that

$$C = 6$$

(4.19)

Five elements, $H, G, O,$ and $R,$ are involved, which $G$ and $R$ are pseudo elements because their internal covalent bonds are not disturbed in the reaction, hence $E = 4$. The maximum number of linearly independent reactions connecting six components spanned by four elements is

$$R = C - E = 6 - 4 = 2$$

(4.20)

which agrees with the proposed reaction scheme.

We now construct the atomic conservation matrix.

<table>
<thead>
<tr>
<th></th>
<th>$H_2O$</th>
<th>$HG$</th>
<th>ROH</th>
<th>$H_3O^+$</th>
<th>$G^-$</th>
<th>$RH_2O^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H$</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>3</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>$G$</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>$O$</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>$R$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
</tr>
</tbody>
</table>

Using elementary row operations,

<table>
<thead>
<tr>
<th></th>
<th>$H_2O$</th>
<th>$HG$</th>
<th>ROH</th>
<th>$H_3O^+$</th>
<th>$G^-$</th>
<th>$RH_2O^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H$</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>−1</td>
</tr>
<tr>
<td>$A$</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>$O$</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>$T$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>−1</td>
<td>1</td>
</tr>
</tbody>
</table>

the last row gives the invariant constraint,

$$x_{H_3O^+} + x_{RH_2O^+} - x_{G^-} = 0$$

(4.21)

where $x_i$ is the mole fraction of component $i$. Eq. (4.21) is the constraint equation for charge neutrality.

Hence, the number of constraints is
\[ I = 1 \]  

At equilibrium, there are two coexisting phases, including the liquid aqueous phase and solid glutamic acid.

\[ P = 2 \]  

As a result, evaluation of the phase rule given in Eq. (2.85) gives

\[ F = C - P - R - I + 2 = 6 - 2 - 2 - 1 + 2 = 3 \]  

The result of phase rule evaluation shows that there are three variables held fixed. Because the temperature and pressure, which are field variables, are fixed experimentally during the dissolution process, one mole fraction, which is a density variable, can be fixed. In the case where one density is fixed, the critical point isomorphism principle predicts the divergence in \( \partial \ln s / \partial (1/T) \) as \( T \to T_c \).

The measurements of glutamic acid solubility, \( s \), are plotted in van’t Hoff form with \( \ln s \ vs. 1/T \) in Fig. 19. It is clear from the figure that the van’t Hoff slope, \( \partial \ln s / \partial (1/T) \) diverges to negative infinity in the critical region.
Figure 19. Van’t Hoff plot of the temperature dependence of the solubility of glutamic (-)-acid in DGME + water
4.8 The Dissolution of Lead Iodide and Sodium Sulfate in IBA and Water Mixture

The simultaneous dissolution of lead iodide and sodium sulfate was performed as a test of the predictive power of the phase rule and isomorphism principle in the case where no critical effect is expected. The reaction scheme of the $PbI_2/Na_2SO_4$ dissolving in the mixture of $IBA + water$ is

\begin{align}
Na_2SO_4(s) & \rightarrow 2Na^+(aq) + SO_4^{2-}(aq) \tag{4.25a} \\
PbI_2(s) & \rightarrow Pb^{2+}(aq) + 2I^-(aq) \tag{4.25b} \\
HA(aq) + H_2O & \rightarrow H_3O^+(aq) + A^-(aq) \tag{4.25c} \\
Pb^{2+}(aq) + SO_4^{2-}(aq) & \rightarrow PbSO_4(s) \tag{4.25d} \\
H_3O^+(aq) + SO_4^{2-}(aq) & \rightarrow HSO_4^-(aq) + H_2O \tag{4.25e}
\end{align}

Based on the above reactions, there are 12 chemical species in the systems. They are: $H_2O$, $HA$, $H_3O^+$, $A^-$, $PbI_2$, $Pb^{2+}$, $SO_4^{2-}$, $PbSO_4$, $I^-$, $Na^+$, $HSO_4^-$, and $Na_2SO_4$. Due to the small amount and high solubility of $Na_2SO_4$ in the solvents, it did not form a separate solid phase. Counting these components, we see that

$$C = 12$$ \tag{4.26}

Seven elements, $H$, $A$, $O$, $Pb$, $S$, $I$, and $Na$, are involved, hence $E = 7$. The maximum number of linearly independent reactions connecting 12 components spanned by seven elements is

$$R = C - E = 12 - 7 = 5$$ \tag{4.27}

which agrees with the proposed reaction scheme.

At chemical equilibrium at a temperature above the critical temperature, there is some solid $PbSO_4$ present as well as some solid $PbI_2$ plus the liquid solution. Therefore, the number of phases is
The invariant constraints of the system can be derived from the atomic conservation matrix,

\[
\begin{array}{c|cccccccccc}
 & Na_2SO_4 & H_2O & HA & PbI_2 & PbSO_4 & H_3O^+ & A^- & Pb^{2+} & SO_4^{2-} & I^- & Na^+ & HSO_4^- \\
\hline
H & 0 & 2 & 1 & 0 & 0 & 3 & 0 & 0 & 0 & 0 & 0 & 1 \\
A & 0 & 0 & 1 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\
O & 4 & 1 & 0 & 0 & 4 & 1 & 0 & 0 & 4 & 0 & 0 & 4 \\
Pb & 0 & 0 & 0 & 1 & 1 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\
I & 0 & 0 & 0 & 2 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\
Na & 2 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\
S & 1 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 1 & 0 & 0 & 1 \\
\end{array}
\]

By eliminating the reactants \(Na_2SO_4, HA, H_2O,\) and \(PbI_2\), the atomic conservation matrix becomes,

\[
\begin{array}{c|cccccccccc}
 & Na_2SO_4 & H_2O & HA & PbI_2 & PbSO_4 & H_3O^+ & A^- & Pb^{2+} & SO_4^{2-} & I^- & Na^+ & HSO_4^- \\
\hline
H & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & \frac{1}{2} & 0 \\
A & 0 & 1 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & -1 \\
O & 0 & 0 & 1 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 4 \\
Pb & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{1}{2} & 0 & 0 \\
I & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 1 & 1 & -\frac{1}{2} & 1 \\
Na & 0 & 0 & 0 & 0 & 0 & 1 & -1 & 2 & -2 & -1 & 1 & -1 \\
S & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 2 & -2 & -1 & 1 & -2 \\
\end{array}
\]

The last two rows without reactants give the constraint equations that are independent of the extent of reaction and independent of the initial conditions,

\[
2x_{Pb^{2+}} - 2x_{SO_4^{2-}} - x_{I^-} + x_{Na^+} - 2x_{HSO_4^-} = 0 \quad (4.29a)
\]

\[
x_{H_3O^+} + 2x_{Pb^{2+}} + x_{Na^+} - x_{I^-} - 2x_{SO_4^{2-}} - x_{HSO_4^-} - x_{A^-} = 0 \quad (4.29b)
\]
where \( x_i \) is the mole fraction of component \( i \). Eq. (4.29a) is the mass constraint stemming from the fact that \( PbSO_4 \) and \( Pb^{2+} \) are produced in stoichiometric amounts because they both come from reactions of \( PbI_2 \) with IBA and sulfate ions. Eq. (4.29b) is the charge neutrality equation for the system. As such, the number of constraints is

\[
I = 2
\]  

(4.30)

As a result, evaluation of the phase rule given in Eq. (2.85) gives

\[
F = C - P - R - I + 2 = 12 - 3 - 5 - 2 + 2 = 4
\]  

(4.31)

Since the phase rule tells us that there are four independent variables in the system, and two of them are temperature and pressure due to the laboratory conditions, the remaining two fixed variables are necessarily component mole fraction variables. The principle of critical point isomorphism predicts that \( (\partial \ln s / \partial (1/T))_{T,P} \) should not diverge at the critical point. After the addition of both solutes, the critical temperature is identified at 305.80 \( K \) by the visual confirmation of critical opalescence. The measurements of lead solubility, \( s \), are plotted in van’t Hoff form with \( \ln s \ vs. 1/T \) in Fig. 20. It is clear from the figure that van’t Hoff slope, \( (\partial \ln s / \partial (1/T)) \) does not diverge in the critical region.
4.9 The Dissolution of Lead Iodide and Lead Sulfate in IBA and Water Mixture

The simultaneous dissolution of lead iodide and lead sulfate follows the reaction scheme

\[ \text{PbSO}_4(s) \rightarrow \text{Pb}^{2+}(aq) + \text{SO}_4^{2-}(aq) \]  \hspace{1cm} (4.32a)
\[ \text{PbI}_2(s) \rightarrow \text{Pb}^{2+}(aq) + 2\text{I}^- (aq) \]  \hspace{1cm} (4.32b)
\[ \text{HA}(aq) + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+(aq) + \text{A}^-(aq) \]  \hspace{1cm} (4.32c)
\[ \text{H}_3\text{O}^+(aq) + \text{SO}_4^{2-}(aq) \rightarrow \text{HSO}_4^-(aq) + \text{H}_2\text{O} \]  \hspace{1cm} (4.32d)
Based on the above reactions, there are 10 chemical species in the systems. They are: $H_2O$, $HA$, $H_3O^+$, $A^-$, $PbI_2$, $Pb^{2+}$, $SO_4^{2-}$, $PbSO_4$, $I^-$ and $HSO_4^-$. Counting these components, we see that

$$C = 10$$  \hspace{1cm} (4.33)

Seven elements, $H, A, O, Pb, S$, and $I$, are involved, hence $E = 6$. The maximum number of linearly independent reactions connecting 10 components spanned by six elements is

$$R = C - E = 10 - 6 = 4$$  \hspace{1cm} (4.34)

which agrees with the proposed reaction scheme.

At chemical equilibrium at a temperature above the critical temperature, there is some solid $PbSO_4$ present as well as some solid $PbI_2$ plus the liquid solution. Therefore, the number of phases is

$$P = 3$$  \hspace{1cm} (4.35)

The invariant constraints of the system can be derived from the atomic conservation matrix.

<table>
<thead>
<tr>
<th></th>
<th>$H_2O$</th>
<th>$HA$</th>
<th>$PbI_2$</th>
<th>$PbSO_4$</th>
<th>$H_3O^+$</th>
<th>$A^-$</th>
<th>$Pb^{2+}$</th>
<th>$SO_4^{2-}$</th>
<th>$I^-$</th>
<th>$HSO_4^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H$</td>
<td>2</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>3</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>$A$</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$O$</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>4</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>4</td>
<td>0</td>
<td>4</td>
</tr>
<tr>
<td>$Pb$</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$I$</td>
<td>0</td>
<td>0</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>$S$</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>1</td>
</tr>
</tbody>
</table>

By eliminating the reactants $HA, H_2O, PbSO_4$, and $PbI_2$, we get

<table>
<thead>
<tr>
<th></th>
<th>$H_2O$</th>
<th>$HA$</th>
<th>$PbI_2$</th>
<th>$PbSO_4$</th>
<th>$H_3O^+$</th>
<th>$A^-$</th>
<th>$Pb^{2+}$</th>
<th>$SO_4^{2-}$</th>
<th>$I^-$</th>
<th>$HSO_4^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H$</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-1</td>
</tr>
<tr>
<td>$A$</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$O$</td>
<td>0</td>
<td>0</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$Pb$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>$I$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>-1</td>
<td>2</td>
<td>-2</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>$S$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>2</td>
<td>-2</td>
<td>-1</td>
<td>-2</td>
<td>-2</td>
</tr>
</tbody>
</table>

97
The last two rows give the constraint equations that both are independent of the extent of reaction and independent of the initial conditions,

\[ x_{H_3O^+} + 2x_{Pb^{2+}} - x_{I^-} - 2x_{SO_4^{2-}} - x_{HSO_4^-} - x_{A^-} = 0 \] (4.36a)

\[ 2x_{Pb^{2+}} - 2x_{SO_4^{2-}} - 2x_{HSO_4^-} - x_{I^-} = 0 \] (4.36b)

where \( x_i \) is the mole fraction of component \( i \). Eq. (4.36a) is the charge neutrality equation in the liquid phase. Eq. (4.36b) is the mass constraint stemming from the fact that \( SO_4^{2-}, HSO_4^- \) and \( I^- \) are produced in stoichiometric amounts because they both come from the dissolution of \( PbSO_4 \). As such, the number of constraints is

\[ I = 2 \] (4.37)

As a result, evaluation of the phase rule given in Eq. (2.85) gives

\[ F = C - P - R - I + 2 = 10 - 3 - 4 - 2 + 2 = 3 \] (4.38)

Since the phase rule tells us that there are three independent variables in the system, and two of them are temperature and pressure due to the laboratory conditions, the remaining one fixed variable is the mole fraction of one component which is a density variable. The principle of critical point isomorphism predicts that \( (\partial \ln s / \partial (1/T)) \) should diverge at the critical point. The measurements of lead solubility, \( s \), are plotted in van’t Hoff form with \( \ln s \ vs. 1/T \) in Fig. 21. It is clear from the figure that van’t Hoff slope, \( (\partial \ln s / \partial (1/T)) \) diverges to negative infinity in the critical region.
Figure 21. Van’t Hoff plot of the temperature dependence of the solubility of lead in IBA + water
4.10 The Dissolution of Barium Sulfate and Calcium Sulfate in IBA and Water Mixture

The dissolution of barium sulfate and calcium is unpublished work by Jason Mote in the UAH Chemical Engineering Honor Bachelor Program. With his permission, we have analyzed these data as a test of the predictive power of the phase rule. The reaction scheme of the $BaSO_4/CaSO_4$ simultaneous dissolving in the mixture of $IBA + water$ is

\[ BaSO_4(s) \rightarrow Ba^{2+}(aq) + SO_4^{2-}(aq) \quad (4.39a) \]

\[ CaSO_4(s) \rightarrow Ca^{2+}(aq) + SO_4^{2-}(aq) \quad (4.39b) \]

\[ HA(aq) + H_2O \rightarrow H_3O^+(aq) + A^-(aq) \quad (4.39c) \]

\[ H_3O^+(aq) + SO_4^{2-}(aq) \rightarrow HSO_4^-(aq) + H_2O \quad (4.39d) \]

Based on the above reactions, there are 10 chemical species in the systems. They are: $H_2O, HA, H_3O^+, A^-, BaSO_4, Ba^{2+}, SO_4^{2-}, CaSO_4, Ca^{2+}$ and $HSO_4^-$. Counting these components, we see that

\[ C = 10 \quad (4.40) \]

Six elements, $H, A, O, Pb, S,$ and $Ca$, are involved, hence $E = 6$. The maximum number of linearly independent reactions connecting 10 components spanned by six elements is

\[ R = C - E = 10 - 6 = 4 \quad (4.41) \]

which agrees with the proposed reaction scheme.

At chemical equilibrium at a temperature above the critical temperature, there is some solid $BaSO_4$ present as well as some solid $CaSO_4$ plus the liquid solution. Therefore, the number of phases is

\[ P = 3 \quad (4.42) \]

The invariant constraints of the system can be derived from the atomic conservation matrix.
By eliminating the reactants \( HA, H_2O, BaSO_4, \) and \( CaSO_4, \) we get

By eliminating the reactants \( HA, H_2O, BaSO_4, \) and \( CaSO_4, \) we get

<table>
<thead>
<tr>
<th>( H_2O )</th>
<th>( HA )</th>
<th>( BaSO_4 )</th>
<th>( CaSO_4 )</th>
<th>( H_3O^+ )</th>
<th>( A^- )</th>
<th>( Ba^{2+} )</th>
<th>( SO_4^{2-} )</th>
<th>( Ca^{2+} )</th>
<th>( HSO_4^- )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( H )</td>
<td>2</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>3</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>( A )</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>( O )</td>
<td>1</td>
<td>0</td>
<td>4</td>
<td>4</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>4</td>
<td>0</td>
</tr>
<tr>
<td>( Ba )</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>( Ca )</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>( S )</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
</tr>
</tbody>
</table>

The last two rows give the constraint equations that both are independent of the extent of reaction and independent of the initial conditions,

\[
x_{H_3O^+} + 2x_{Ba^{2+}} + 2x_{Ca^{2+}} - 2x_{SO_4^{2-}} - x_{HSO_4^-} - x_{A^-} = 0 \quad (4.43a)
\]

\[
x_{Ba^{2+}} + x_{Ca^{2+}} - x_{SO_4^{2-}} - x_{HSO_4^-} = 0 \quad (4.43b)
\]

where \( x_i \) is the mole fraction of component \( i. \) Eq. (4.43a) is the charge neutrality equation in the liquid phase. Eq. (4.43b) is the mass constraint stemming from the fact that \( SO_4^{2-} \) and \( HSO_4^- \) are produced in stoichiometric amounts because they both come from the dissolution of \( BaSO_4 \) and \( CaSO_4. \) As such, the number of constraints is

\[
I = 2 \quad (4.44)
\]

As a result, evaluation of the phase rule given in Eq. (2.85) gives

101
\[ F = C - P - R - I + 2 = 10 - 3 - 4 - 2 + 2 = 3 \]

Since the phase rule tells us that there are three independent variables in the system, and two of them are temperature and pressure due to the laboratory conditions, the remaining one fixed variable is the mole fraction of one component which is a density variable. The principle of critical point isomorphism predicts that \((\partial \ln s / \partial (1/T))\) should diverge at the critical point. In this experiment, the solubilities of barium and calcium were measured and plotted in van’t Hoff form with \(\ln s \ vs. 1/T\) in Fig. 22 and Fig. 23, respectively. It is clear from the figures that van’t Hoff slope, \((\partial \ln s / \partial (1/T))\) diverges in the critical region for both elements.

Figure 22. Van’t Hoff plot of the temperature dependence of the solubility of barium in IBA + water mixture. The standard concentrations of barium, \(s^0 = 0.005\mu g/mL\)
Figure 23. Van’t Hoff plot of the temperature dependence of the solubility of calcium in IBA + water mixture. The standard concentrations of calcium, $s^0 = 1\mu g/mL$. 
4.11 The Dissolution of Zinc (+)-Tartrate and Zinc (-)-Tartrate in IBA + Water Mixture

A strong critical effect on the solubility of zinc is expected in the dissolution of zinc (+)-tartrate and zinc (-)-tartrate in the IBA + water mixture. Because zinc (+)-tartrate and zinc (-)-tartrate are enantiomers, despite they have different molecule structures, as shown in Fig. 24, their solubilities and reaction rates are the same in a non-chiral system. Therefore, the reaction scheme is the same as the dissolution of zinc (-)-tartrate in the IBA + water mixture,

\[
\begin{align*}
HA(aq) + H_2O & \rightarrow H_3O^+(aq) + A^-(aq) \\
ZnT(s) & \rightarrow Zn^{2+}(aq) + T^{2-}(aq)
\end{align*}
\]

Since neither IBA nor water is chiral, (+)-tartrate ions and (-)-tartrate ions are chemically identical in the mixture, there are seven components, including \(H_2O, HA, H_3O^+, A^-, Zn^{2+}, T^{2-}\), and \(ZnT\), where \(T\) represents the tartrate ion. Hence,

\[C = 7\]  \hspace{1cm} (4.46)

Five elements, \(H, A, O, Zn,\) and \(T\), are involved, which \(A\) and \(T\) are pseudo elements because their internal covalent bonds are not disturbed in the reaction, hence \(E = 5\).
The maximum number of linearly independent reactions connecting seven components spanned by five elements is

\[ R = C - E = 7 - 5 = 2 \]  

which agrees with the proposed reaction scheme.

In addition, the number of invariant constraints in the system is also the same as the dissolution of zinc (-)-tartrate as calculated in section VI of this chapter.

\[ I = 2 \]

However, the undissolved zinc (+)-tartrate and zinc (-)-tartrate are treated as different solid phases because of their different physical properties. Thus, including the liquid phase, there are three coexisting phases at the chemical equilibrium,

\[ P = 3 \]

Evaluation of the generalized phase rule given in Eq. (2.85), we obtain

\[ F = C - P - R - I + 2 = 7 - 3 - 2 - 2 + 2 = 2 \]

Since temperature and pressure are fixed due to the experiment condition, Eq. (4.50) suggests that there are no fixed density variables. As a result, the critical point isomorphism principle predicts a strong divergence in \( \partial \ln s / \partial (1/T) \) as \( T \to T_c \) in the dissolution of zinc (+)-tartrate and zinc (-)-tartrate in the IBA + water mixture. The measurements of zinc solubility, \( s \), are plotted in van’t Hoff form with \( \ln s \ vs. \ 1/T \) in Fig.16. It is clear from the figure that the van’t Hoff slope, \( \partial \ln s / \partial (1/T) \) diverges to positive infinity in the critical region.
Figure 25. Van’t Hoff plot of the temperature dependence of the solubility of zinc in the IBA + water
4.12 Discussion

In each of the experiments above, the measurements of solubility are plotted in the form \( \ln s \) vs. \( 1/T \). The solubility data collected outside the critical region, which is a straight line, can be fitted by the van’t Hoff equation,

\[
\ln s = -\frac{\Delta H}{RT} + \frac{\Delta S}{R}
\]

where \( R \) and \( \Delta S \) are the gas constant and dissolution entropy, respectively. When a solubility critical effect occurs, \( i.e., \ F < 4 \), the data collected within the critical region diverges from the extrapolation of the straight line, and the direction of divergence within the critical region is determined by Eq. (3.37)

\[
\left( \frac{\partial \ln s}{\partial (1/T)} \right)_P = -T\Delta H \left( \frac{\partial \ln s}{\partial \Delta G} \right)_{T,P}
\]

where \( \partial \ln s / \partial \Delta G \) is positive due to the requirement of thermodynamic stability. Therefore, both signs of the slope outside the critical region and the divergence inside the critical region are consistent and depend on the sign of the dissolution enthalpy. This means for an exothermic dissolution for which \( \Delta H > 0 \), such as phenolphthalein, barium chromate, zinc tartrate, glutamic acid, and barium sulfate, both directions of the slope of van’t Hoff equation and the divergence in the critical region are negative. In contrast, they should be positive in an endothermic dissolution for which \( \Delta H < 0 \), such as gallium oxide, lead iodide, and calcium sulfate. It should be noted that the different directions of the divergence in the solubility of barium and calcium in the simultaneous dissolution of barium sulfate and calcium sulfate reveal a potential interesting method to separate substances from a mixture by the critical point phenomenon.

The phase rule analysis of the dissolution of \( PbI_2 \) and \( Na_2SO_4 \) in IBA + water mixture results in \( F = 4 \). The fixed variables are two fields, temperature and pressure, and the two fixed density variables,
the mole fractions of IBA and $Na_2SO_4$. Based on the Griffiths-Wheeler rule, the critical effect on the solubility of lead should not be expected when there is more than one fixed density variable. This conclusion is substantiated by the solubility data as shown in Fig. 19.

The weak critical effect on the solubility is predicted by the Griffiths-Wheeler rule when only one density variable is held fixed. Thus, the number of independent variables equals three, $F = 3$, because temperature and pressure are fixed under experimental conditions. This prediction is proven by the solubility data that we have obtained in the case of the seven dissolution experiments, phenolphthalein (Fig. 13), barium chromate (Fig. 14), gallium oxide (Fig. 15), zinc (-)-tartrate (Fig. 16), glutamic (+)-acid (Fig. 18), lead iodide + lead sulfate (Fig. 20), and barium sulfate + calcium sulfate (Fig. 20), each of which shows the weak divergence in the critical region. Those solubility measurements validate the predictive power of the phase rule and isomorphism principal analysis for the case of $F = 3$ in various systems such as chemical inert solute (phenolphthalein), single metal salt (barium chromate and gallium oxide), organic solute (zinc tartrates and glutamic acid), and complex simultaneous dissolution (lead iodide + lead sulfate and barium sulfate + calcium sulfate). One shall note that the dissolution of glutamic acid in DGME + water is the acidic solute dissolving in the basic solvent, which distinguishes it from the other solutes in IBA + water, in all of which the acid role is played by the solvent. Moreover, the DGME + Water is characterized by a lower critical solution temperature (LCST), in contrast to the other two binary mixtures (IBA/water and nitrobenzene/dodecane), all of which have upper critical soliton temperature (UCST). As a result, the application of the phase rule and isomorphism principal analysis for the critical solubility effect has been expanded from the metal oxides and simple salts dissolving in IBA + Water [20-26] to more comprehensive systems.
The simultaneous dissolution of zinc (+)-tartrate and zinc (-)-tartrate in IBA + water is the first case in which a strong critical effect on the solubility is proposed and observed. Compared with the dissolution of zinc (-)-tartrate, the addition of zinc (+)-tartrate to the system increases the number of coexisting phases by one, which is solid zinc (+)-tartrate and zinc (-)-tartrate, but it maintains the number of components and reactions because they are chemically identical in the non-chiral environment. Hence, due to Eq. (4.50), the value of $F$ is decreased by one, $F = 2$, and the strong critical effect on solubility is predicted. The comparison of solubility data of zinc from both dissolutions is given in Fig. 26. Although
the zinc measurements are not precise enough to compare the critical exponent of solubility, it is clear that
the solubility of zinc for the $F = 2$ case, which is represented by open circles, divergence is steeper than
that, which is represented by the solid squares, for the $F = 3$ case.

The phase rule appears to be a satisfactory method for classifying critical effects in the dissolution
of solids in liquid binary mixtures. The solutes and solvents are selected from distinctive natures to prove
the isomorphism principle of critical point phenomena. The results for all reported systems are
summarized in Table. 5. Since the generalized phase rule is a powerful tool to encounter the number of
independent intensive variables without knowing the exact chemical process, it makes Griffiths-Wheeler
rule practical for predicting the critical effect in complex heterogeneous chemical equilibria.

<table>
<thead>
<tr>
<th>No</th>
<th>Solute</th>
<th>Solvent</th>
<th>$F$</th>
<th>Dissolution Enthalpy</th>
<th>Critical Effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Phenolphthalein</td>
<td>Nitrobenzene/Dodecane</td>
<td>3</td>
<td>Exothermic</td>
<td>Weak</td>
</tr>
<tr>
<td>2</td>
<td>BaCrO$_4$</td>
<td>IBA/Water</td>
<td>3</td>
<td>Exothermic</td>
<td>Weak</td>
</tr>
<tr>
<td>3</td>
<td>Ga$_2$O$_3$</td>
<td>IBA/Water</td>
<td>3</td>
<td>Endothermic</td>
<td>Weak</td>
</tr>
<tr>
<td>4</td>
<td>Zinc (-)-tartrate</td>
<td>IBA/Water</td>
<td>3</td>
<td>Exothermic</td>
<td>Weak</td>
</tr>
<tr>
<td>5</td>
<td>Glutamic (+)-acid</td>
<td>DGME/Water</td>
<td>3</td>
<td>Exothermic</td>
<td>Weak</td>
</tr>
<tr>
<td>6</td>
<td>PbI$_2$/Na$_2$SO$_4$</td>
<td>IBA/Water</td>
<td>4</td>
<td>Endothermic</td>
<td>None</td>
</tr>
<tr>
<td>7</td>
<td>PbI$_2$/PbSO$_4$</td>
<td>IBA/Water</td>
<td>3</td>
<td>Endothermic</td>
<td>Weak</td>
</tr>
<tr>
<td>8</td>
<td>BaSO$_4$/CaSO$_4$</td>
<td>IBA/Water</td>
<td>3</td>
<td>Exothermic (Ba)/Endothermic (Ca)</td>
<td>Weak</td>
</tr>
<tr>
<td>9</td>
<td>Zinc (+)-tartrate/Zinc (-)-tartrate</td>
<td>IBA/Water</td>
<td>2</td>
<td>Exothermic</td>
<td>Strong</td>
</tr>
</tbody>
</table>

Table 5. Summary of the critical phenomena in solids dissolving in liquid binary mixtures.
The critical opalescence in binary liquid mixtures has been interpreted by the regular solution model in chapter 3. In this chapter, we will use the phase rule and isomorphism principle to analyze the critical opalescence in multicomponent systems. By counting the number of independent variables describing the multicomponent system, we predict that the critical opalescence will be suppressed when a solute is added no matter the nature of the solute.

5.1 Experimental Materials

Because the critical opalescence is associated with the fluctuation of refractive indices of the medium, six binary mixture systems with various values of relative indices were selected for our investigation. The solutes are chosen because of their high solubility in the mixture which serves to prevent the formation of a possible solid phase. Only a trace amount of solutes was added to minimize the shift to the critical temperature. Table 6 below summarizes the critical points and refractive indices of selected binary mixtures. The liquid mixture systems examined for the critical opalescence were (1) nitrobenzene + dodecane, (2) methanol + hexene, (3) 2,6-lutidine + water, (4) IBA + water, (5) ethylene glycol (EG) +
nitromethane (NM), (6) 1-nonanol (1N) + NM, (7) EG + 1N. Systems (1)-(4) were used to test the suppression of critical opalescence by the addition of cholesterol and sodium chloride, which are solids. In systems (5) and (6), the critical opalescence was suppressed by the addition of 1-dodecanol and EG which are liquids. System (7) is a test of the dependence of the critical opalescence on the refractive indices of the solvent components. The mixture of 2,6-lutidine + water is characterized by a lower critical solution temperature (LCST), which is different from the other mixtures, all of which have upper critical solution temperature (UCST). Isobutyric acid (99+%), nitrobenzene (99+%), dodecane (99%), 2,6-lutidine (99.0%), and nitromethane (99+%) were obtained from Acros Organics. Methanol (99.9%) and hexene (99.0%) were obtained from Alfa Aesar. 1- dodecanol (>99.0%) and 1-nonanol (>99.0%) were obtained from TCI chemicals. Ethylene glycol (99.8%) was obtained from Fisher chemical. Cholesterol (99+%) and sodium chloride (99%) were obtained from Sigma-Aldrich. All chemicals were used without further purification. Water was distilled once from a glass system. The binary mixture was prepared at the critical mass fraction by weighting.

Table 6. Summary of selected binary mixtures and solutes

<table>
<thead>
<tr>
<th>No</th>
<th>Solute</th>
<th>Solvent</th>
<th>Critical point</th>
<th>n₁</th>
<th>n₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cholesterol</td>
<td>Nitrobenzene/Dodecane</td>
<td>UCST</td>
<td>1.556 [44]</td>
<td>1.422 [45]</td>
</tr>
<tr>
<td>2</td>
<td>Cholesterol</td>
<td>Methanol/Hexene</td>
<td>UCST</td>
<td>1.329 [46]</td>
<td>1.373 [46]</td>
</tr>
<tr>
<td>3</td>
<td>NaCl</td>
<td>2,6-lutidine /water</td>
<td>LCST</td>
<td>1.495 [44]</td>
<td>1.333 [47]</td>
</tr>
<tr>
<td>4</td>
<td>NaCl</td>
<td>IBA/Water</td>
<td>UCST</td>
<td>1.393 [46]</td>
<td>1.333 [47]</td>
</tr>
<tr>
<td>5</td>
<td>1D</td>
<td>EG/NM</td>
<td>UCST</td>
<td>1.432 [45]</td>
<td>1.382 [45]</td>
</tr>
<tr>
<td>6</td>
<td>EG</td>
<td>1N/NM</td>
<td>UCST</td>
<td>1.434 [46]</td>
<td>1.382 [45]</td>
</tr>
<tr>
<td>7</td>
<td>N/A</td>
<td>EG/1N</td>
<td>UCST</td>
<td>1.432 [45]</td>
<td>1.434 [46]</td>
</tr>
</tbody>
</table>
5.2 Experimental Methods

The turbidity was measured using the apparatus in Fig. 27. Unpolarized Light from a 632.8 nm He-Ne laser (JDS Uniphase, 1135) passed through an attenuator and was split by the beam splitter into two beams, one passing through the binary mixture and another providing a reference. Light intensities of both beams were measured by an optical power meter (Newport, 1830c). Although the turbidity was originally computed by integrating over all scattered angles [48], we find that it’s more convenient to calculate it by measuring the intensity of transmitted light,

\[ \tau^* = -\ln(I/I_0)/L \]  \hspace{1cm} (5.1)

where \( I \) is the intensity of transmitted light, \( I_0 \) is the intensity of reference light, and \( L \) is the diameter of the test tube.

Figure 27. Schematic diagram of apparatus: HL, helium-neon laser; A, attenuator; BS, beam splitter; M, mirror; WB, water bath; T, test tube; PM, optical power meter.
Binary mixtures were prepared in 30-mm-i.d., flat bottom Pyrex test tubes. Each test tube contained a magnetic spin bar. The temperature of test tubes and their contents were controlled to within \( \pm 10 \text{ mK} \) using a water bath with a thermostat. A digital platinum resistance thermometer was used to measure differences in temperature with a precision of \( \pm 0.007 \text{ K} \). The details of the thermostat system were previously described in Chapter 4.

In the beginning, the bath temperature was set in the single-phase region far away from the critical temperature. The binary mixture was stirred continuously for 15 minutes after the bath temperature was stable and turned off for an additional 15 minutes to reach the phase equilibrium. After the intensities of the transmitted beam and the reference beam were measured, the thermostat temperature was adjusted closer to the critical temperature, and the process of stir-set was repeated. The thermostat temperature was first changed by 0.5 K over the range of \( |T - T_c| > 1.5 \text{ K} \). In the vicinity of the critical point, the binary mixture was taken from the single-phase region into the two-phase region in a sequence of 0.05 K temperature steps. At the end of data collection, the critical temperature was confirmed by the visual observation of phase separation. In the critical region, the process of spontaneous phase separation may take hours to complete, however, the top and bottom of the contents will start to turn transparent a few minutes after the stir was turned off.

The bath temperature was then reset, and only a small amount, to prevent the creation of a new phase, solute was added to the binary mixture and the resulting shift in the critical temperature was determined. The process of data collection was repeated for this particular mixture. By following this method, we determined the temperature dependence of the turbidity for the four mixtures before and after the solute was added.
5.3 The Suppression of Critical Opalescence in Binary Mixtures

5.3.1 The Effect of Refractive Indices

In the critical region of binary mixtures, the turbidity is associated with the statistical variance in the relative permittivity,

\[ \tau^* = \frac{8\pi^3}{3\lambda^4} (\langle \Delta \varepsilon_r \rangle^2) \nu \]

In Chapter 3, we show that the variance \( (\langle \Delta \varepsilon_r \rangle^2) \) is proportional to thermodynamic derivatives \( (\partial x_i/\partial \mu_i) \) which will diverge at the critical point if the system does not contain more than one fixed density.

In the case of a chemically inert binary liquid mixture, there are two components, so

\[ C = 2 \]

There is only one liquid phase at the critical point, so

\[ P = 1 \]

Because solvent components are inert with respect to one another, both the number of reactions,

\[ R = 0 \]

and the number of constraints

\[ I = 0 \]

According to Eq. (2.85), the number of independent variables is

\[ F = C - P - R - I + 2 = 2 - 1 - 0 - 0 + 2 = 3 \] \hspace{1cm} (5.2)
Two of these are temperature and pressure, which are fields; the remaining variable is the molar concentration of component \( i \), \( x_i \), which is a density. Hence, the derivative of a density with respect to a field, \( (\partial x_i / \partial \mu_i) \), diverges at the critical point,

\[
\tau^*_{T \to T_c} \sim (\partial x_i / \partial \mu_i) \to \infty
\]

which implies critical opalescence is expected.

Also, at optical frequencies, we can make the replacement,

\[
\varepsilon_r = n^2
\]

where \( n \) is the refractive index. Hence,

\[
\langle (\Delta \varepsilon_r)^2 \rangle \sim \langle (\Delta n)^2 \rangle
\]

In the case of the binary mixture in which the two components have distinct refractive indices, in the critical region, the fluctuations in \( \Delta n \) are enlarged by the divergence of \( (\partial x_i / \partial \mu_i) \) which causes the critical opalescence. However, if the refractive indices of both components are so close, \( \Delta n \to 0 \), the critical opalescence disappears despite the occurrence of fluctuations.

A comparison of the turbidity measurements of chemically inert binary mixtures of 1N + EG and the NM + EG are shown in Fig. 28. According to the phase rule analysis predictions, fluctuations are expected in both mixtures. However, because the refractive indices in the 1N + EG mixture are almost
identical (see Table. 6), opalescence is missing in this mixture. By contrast, opalescence is observed in the NM + EG mixture where the indices are not matched. These behaviors are clearly evident in Fig. 28.

Figure 28. Temperature dependence of turbidity of binary mixtures of nitromethane (NM) + ethylene glycol (EG) and 1-nonanol (1N) + ethylene glycol (EG)
5.3.2 The Effect of an Inert Solid

In this section, we will show that even in the case of distinct refractive indices, the critical opalescence still can be suppressed upon the addition of a small amount of solute into the binary mixture. After the addition of a solute, there are three components,

\[ C = 3 \]

The number of coexisting phases remains one because the solute is dissolved completely

\[ P = 1 \]

The solute is also chemically inert with respect to both solutes, the number of reactions

\[ R = 0 \]

So does the number of constraints

\[ I = 0 \]

According to Eq. (2.85), the number of independent variables is

\[ F = C - P - R - I + 2 = 3 - 1 - 0 - 0 + 2 = 4 \] (5.3)

Besides the temperature and pressure, which are fields, there are two molar concentrations, which are densities, that remain fixed. As a result, the derivative of a density with respect to a field, \((\partial x_i / \partial \mu_i)\), should be finite at the critical point, implying that the critical opalescence is suppressed.
The measurements of turbidity, $\tau^*$, as a function of the temperature are plotted in Fig. 29 (nitrobenzene + dodecane) and Fig. 30 (methanol + hexene). It is clear from the figure that the turbidity of mixtures without solutes diverges in the critical region. The divergence observed in the binary mixture is suppressed by the addition of $10^{-2} M$ cholesterol.

Figure 29. Temperature dependence of turbidity from nitrobenzene (CH$_3$NO$_2$) + dodecane (C$_{12}$H$_{26}$) w/wo cholesterol.
Figure 30. Temperature dependence of turbidity from methanol (CH$_3$OH) + hexene (C$_6$H$_{14}$) w/wo cholesterol.

5.3.3 The Effect of a Reactive Solid

5.3.3.1 IBA + water + NaCl

A chemical reaction is supported by the mixture of IBA + water,

\[ HA(aq) + H_2O \rightarrow H_3O^+(aq) + A^-(aq) \] (5.4)

where HA represents isobutyric acid and A$^-$ represents the isobutyrate ion. There are four components: HA, $H_2O$, $H_3O^+$, and $A^-$; so $C = 4$. Three elements, $H$, $A$, and $O$, are involved, which $A$ is a pseudo element because its internal covalent bonds are not disturbed in the reaction, hence
\[ E = 3 \quad (5.5) \]

The maximum number of linearly independent reactions connecting four components spanned by three elements is

\[ R = C - E = 4 - 3 = 1 \quad (5.6) \]

which agrees with Eq. (5.4).

The number of coexisting phases remains one at the critical point, so

\[ P = 1 \quad (5.7) \]

The invariant constraints of the system can be derived from the atomic conservation matrix.

\[
\begin{array}{c|cccc}
 & H_2O & HA & H_3O^+ & A^- \\
\hline
H & 2 & 1 & 3 & 0 \\
A & 0 & 1 & 0 & 1 \\
O & 1 & 0 & 1 & 0 \\
\end{array}
\]

Using elementary row operations,

\[
\begin{array}{c|cccc}
 & H_2O & HA & H_3O^+ & A^- \\
\hline
H & 1 & 0 & 0 & 1 \\
A & 0 & 1 & 0 & 1 \\
O & 0 & 0 & 1 & -1 \\
\end{array}
\]

the last row without the reactants \( H_2O \) and \( HA \) gives the invariant constraint that is independent of the extent of reaction and independent of the initial conditions,

\[ x_{H_2O^+} - x_{A^-} = 0 \quad (5.8) \]

where \( x_i \) is the mole fraction of component \( i \). Eq. (5.7) expresses charge neutrality in the liquid phase.

Thus, the number of invariant constraints in the system is given by

\[ I = 1 \quad (5.9) \]

Evaluation of the generalized phase rule given in Eq. (2.85), we obtain
\[ F = C - P - R - I + 2 = 4 - 1 - 1 - 1 + 2 = 3 \]  \hspace{1cm} (5.10)

Despite the mixture of IBA + water being chemically reactive, it is still described by \( F = 3 \), which places it in the same phase rule group as chemically inert mixtures where critical opalescence is expected. The divergence in the turbidity of IBA + water as \( T \to T_c \) is shown in Fig. 31 (solid squares).

![Figure 31. Temperature dependence of turbidity from isobutyric acid + water w/wo NaCl.](image)

Upon addition of a small amount of NaCl, there are six components: \( HA, H_2O, H_3O^+, A^-, Na^+, \) and \( Cl^- \).

\[ C = 6 \]  \hspace{1cm} (5.11)
Five elements, $H, A, O, Na$, and $Cl$, are now involved, which $A$ is a pseudo element because its internal covalent bonds are not disturbed in the reaction, hence

$$E = 5$$ \hspace{1cm} (5.12)

The maximum number of linearly independent reactions connecting six components spanned by four elements is

$$R = C - E = 6 - 5 = 1$$ \hspace{1cm} (5.13)

Thus, the reaction scheme is the same

$$HA(aq) + H_2O \rightarrow H_3O^+(aq) + A^-(aq)$$ \hspace{1cm} (5.14)

The atomic conservation matrix becomes,

<table>
<thead>
<tr>
<th></th>
<th>$H_2O$</th>
<th>$HA$</th>
<th>$NaCl$</th>
<th>$H_3O^+$</th>
<th>$A^-$</th>
<th>$Na^+$</th>
<th>$Cl^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H$</td>
<td>2</td>
<td>1</td>
<td>0</td>
<td>3</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$A$</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$O$</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$Na$</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>$Cl$</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Using elementary row operations,

<table>
<thead>
<tr>
<th></th>
<th>$H_2O$</th>
<th>$HA$</th>
<th>$NaCl$</th>
<th>$H_3O^+$</th>
<th>$A^-$</th>
<th>$Na^+$</th>
<th>$Cl^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H$</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$A$</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$O$</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>$Na$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>-1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$Cl$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
</tr>
</tbody>
</table>

the last two rows without the reactants $H_2O$, $HA$, and $NaCl$ give invariant constraints that are independent of the extent of reaction and independent of the initial conditions,

$$x_{H_3O^+} - x_{A^-} = 0$$ \hspace{1cm} (5.15a)

$$x_{H_3O^+} - x_{A^-} + x_{Na^+} - x_{Cl^-} = 0$$ \hspace{1cm} (5.15b)
where \( x_i \) is the mole fraction of component \( i \). Eqs. (5.15) express the constraints of mass conservation and charge neutrality in the liquid phase. Thus, the number of invariant constraints in the system is given by

\[
I = 2
\]  

(5.16)

Evaluation of the generalized phase rule given in Eq. (2.85), we obtain

\[
F = C - P - R - I + 2 = 6 - 1 - 1 - 2 + 2 = 4
\]  

(5.17)

Since the field variables, \( T \) and \( P \), are fixed by the experiment conditions, \( F = 4 \) implies that two mole fractions will be fixed. According to the Griffiths-Wheeler rule, the derivative \( (\partial x_i / \partial \mu_i) \) will not exhibit a critical effect, and thus the turbidity will not diverge in the critical region. This prediction is proven in Fig. 31 (open circles).

### 5.3.3.2 2,6-lutidine + water + NaCl

In the previous example, the phase rule analysis successfully predicts the suppression of the critical opalescence in a binary mixture with upper critical solution temperature (UCST). Although the principle of critical point isomorphism suggests that the method applies to different systems in the same universality class, it is still necessary to test our method in the system with lower critical solution temperature (LCST), \( e.g. \), 2,6-lutidine + water, see Fig. 32.
The mixture of 2,6-lutidine + water supports the chemical reaction

$$RN(aq) + H_2O \rightarrow RNH^+(aq) + OH^-(aq)$$  \hspace{1cm} (5.18)

where $RN$ represents the 2,6-lutidine. There are four components: $RN$, $H_2O$, $RNH^+$, and $OH^-$; so $C = 4$. Three elements, $RN$, $O$, and $H$, are involved, which $RN$ is a pseudo element because its internal covalent bonds are not disturbed in the reaction, hence

$$E = 3$$  \hspace{1cm} (5.19)

The maximum number of linearly independent reactions connecting four components spanned by three elements is

$$R = C - E = 4 - 3 = 1$$  \hspace{1cm} (5.20)

which agrees with Eq. (5.18).

Figure 32. The phase diagram of 2,6-lutidine + water [49]
The number of coexisting phases remains one at the critical point, so

\[ P = 1 \]  \hspace{1cm} (5.21)

The invariant constraints of the system can be derived from the atomic conservation matrix.

\[
\begin{array}{cccc}
RN & H_2O & RNH^+ & OH^- \\
RN & 0 & 1 & 1 & 0 \\
H & 2 & 0 & 1 & 1 \\
O & 1 & 0 & 0 & 1
\end{array}
\]

Using elementary row operations,

\[
\begin{array}{cccc}
RN & H_2O & RNH^+ & OH^- \\
RN & 1 & 0 & 0 & 1 \\
H & 0 & 1 & 0 & 1 \\
O & 0 & 0 & 1 & -1
\end{array}
\]

the last row gives the invariant constraint that is independent of the extent of reaction and independent of the initial conditions,

\[ x_{RNH^+} - x_{OH^-} = 0 \]  \hspace{1cm} (5.22)

where \( x_i \) is the mole fraction of component \( i \). Eq. (5.22) expresses charge neutrality in the liquid phase. Thus, the number of invariant constraints in the system is given by

\[ I = 1 \]  \hspace{1cm} (5.23)

Evaluation of the generalized phase rule given in Eq. (2.85), we obtain

\[ F = C - P - R - I + 2 = 4 - 1 - 1 - 1 + 2 = 3 \]  \hspace{1cm} (5.24)

Despite its critical solution temperature and chemical reactions being different from the mixture of IBA + water, the phase rule analysis gives the same result for the mixture of 2,6-lutidine + water and critical opalescence is expected. The divergence in the turbidity of 2,6-lutidine + water as \( T \to T_c \) is shown in Fig. 33 (solid squares).
Figure 33. Temperature dependence of turbidity from 2,6-lutidine + water w/wo NaCl.

Upon addition of a small amount of NaCl, there are six components: \( RN, H_2O, RNH^+, OH^-, Na^+, \)
and \( Cl^- \),

\[
C = 6
\]  \hspace{1cm} (5.25)

Five elements, \( H, O, RN, Na, \) and \( Cl \), are now involved, which \( RN \) is a pseudo element because its internal covalent bonds are not disturbed in the reaction, hence

\[
E = 5
\]  \hspace{1cm} (5.26)
The maximum number of linearly independent reactions connecting six components spanned by four elements is

\[ R = C - E = 6 - 5 = 1 \]  \hspace{1cm} (5.27)

Thus, the reaction scheme does not change,

\[ RN(aq) + H_2O \rightarrow RNH^+(aq) + OH^-(aq) \]  \hspace{1cm} (5.28)

The atomic conservation matrix becomes,

\[
\begin{array}{ccccccc}
H & 2 & 0 & 0 & 1 & 1 & 0 & 0 \\
O & 1 & 0 & 0 & 0 & 1 & 0 & 0 \\
RN & 0 & 1 & 0 & 1 & 0 & 0 & 0 \\
Na & 0 & 0 & 1 & 0 & 0 & 1 & 0 \\
Cl & 0 & 0 & 1 & 0 & 0 & 0 & 1 \\
\end{array}
\]

Using elementary row operations,

\[
\begin{array}{ccccccc}
H & 1 & 0 & 0 & 0 & 1 & 0 & 0 \\
O & 0 & 1 & 0 & 0 & 1 & 0 & 0 \\
RN & 0 & 0 & 1 & 0 & 0 & 0 & 1 \\
Na & 0 & 0 & 0 & 1 & -1 & 0 & 0 \\
Cl & 0 & 0 & 0 & 1 & -1 & 1 & -1 \\
\end{array}
\]

the last two rows without the reactants \( H_2O \), \( RN \), and \( NaCl \) give invariant constraints that are independent of the extent of reaction and independent of the initial conditions,

\[ x_{RNH^+} - x_{OH^-} = 0 \]  \hspace{1cm} (5.29a)

\[ x_{RNH^+} - x_{OH^-} + x_{Na^+} - x_{Cl^-} = 0 \]  \hspace{1cm} (5.29b)

where \( x_i \) is the mole fraction of component \( i \). Eqs. (5.29) express the constraints of mass conservation and charge neutrality in the liquid phase. Thus, the number of invariant constraints in the system is given by

\[ l = 2 \]  \hspace{1cm} (5.30)
Evaluation of the generalized phase rule given in Eq. (2.85), we obtain

\[ F = C - P - R - I + 2 = 6 - 1 - 1 - 2 + 2 = 4 \]  \hspace{1cm} (5.31)

Thus, the turbidity will not diverge in the critical region, as shown in Fig. 33 (open circles), because the addition of NaCl introduces an extra density variable which is the mole fraction of NaCl.

### 5.4 The Critical Opalescence in Ternary Liquid Mixtures

The phase rule and critical point isomorphism principle suggest that the critical opalescence will not happen at the tri-critical point of ternary mixtures. In particular, for a chemically inert ternary liquid mixture, there are three components, so \( C = 3 \). There is only one liquid phase at the tri-critical point, so \( P = 1 \). Because all components are chemically inert to each other, both the number of reactions and the number of constraints equal zero, \( R = 0 \) and \( I = 0 \), respectively. According to Eq. (2.85), the number of independent variables is thus \( F = 4 \). Like other \( F = 4 \) cases, there are two fixed field variables, \( T \) and \( P \), and two fixed density variables, \( x_1 \) and \( x_2 \). Thus, the derivative of a density with respect to a field, \( \frac{\partial x_i}{\partial \mu_i} \), is finite in the critical region, in which the critical opalescence is not expected at the tri-critical point.

In order to prevent the formation of the micro-heterogeneous phase caused by the clustering of molecules and ions [50] and minimize the shift in the shape of the coexistence surface, only a trace amount of 1D was introduced into the mixture of EG + NM. The turbidities of ternary mixtures of EG + NM + 1D are measured and shown as a function of \( |T - T_c| \) in graphical form in Fig. 34. We also measured the turbidity at the critical point of EG + NM as the reference. It is clear from the figure that the turbidity of
the mixture of EG + NM + 1D remains finite which agrees with the prediction of the disappearance of critical opalescence at the tri-critical point.

Figure 34. Temperature dependence of turbidity from ethylene glycol (EG) + nitromethane (NM) w/wo 1-dodecanol (1D).

According to the principle of critical point isomorphism, the critical opalescence is absent at the tri-critical point for all ternary mixtures. This conclusion was tested by measuring the turbidity at the tri-critical point of the mixture of 1N + NM + EG. Because there are only small amounts of EG in the mixture and all three components are chemically inert with respect to one another, the number of independent
variables is $F = 4$. The critical opalescence is thus not expected at the tri-critical point of the mixture of 1N + NM + EG, as shown in Fig. 35.

Figure 35. Temperature dependence of turbidity from 1-nonanol (1N) + nitromethane (NM) w/wo ethylene glycol (EG).
5.5 Discussion

In each of the experiments above, the measurements of turbidity are plotted in the form $\tau^* \text{ vs. } |T - T_c|$. It is clear from Fig. 28 that the critical opalescence can be reduced in a system where the refractive indices of the two liquid components are very close to each other. It provides opportunities to investigate the microstructural change at the critical point by using optical measurement methods, such as optical rotation, UV-Vis spectroscopy, X-ray diffraction spectroscopy, etc. We find that the refractive indices of 1N and EG are so close that the critical opalescence vanishes for this binary mixture, which makes it an ideal system to explore the critical phase transition of binary mixtures.

Although the data from our experiments are insufficiently precise to compute an accurate numerical value for the critical exponent of the turbidity to describe its divergence in the critical region, the result of turbidity measurements, see Figs. 28 – 32, clearly proves our prediction made by the phase rule analysis that the critical opalescence of the binary mixture will be suppressed upon the addition of a completely dissolved solute. Moreover, the wide selection of binary mixtures and solutes confirms the isomorphism principle that the suppression of critical opalescence should be observable in the case of any solute dissolving in any one of thousands of binary liquid mixtures known to have a critical point of solution.

The result of turbidity measurements of two ternary mixtures, as shown in Figs. 33 and 34, shows the application of the phase rule and isomorphism principal analysis is not limited to the binary mixture but also generalized to multicomponent systems such as the ternary system. Although the critical opalescence is not expected at the tri-critical point of ternary mixtures, it has been observed in some ternary liquid mixtures, such as 3-methylpyridine (3MP) + water + NaBr \cite{27,55–68}. There has been some debate as to whether a micro-heterogeneous phase exists or not above the tri-critical point of those
ternary mixtures [51–74]. According to the phase rule and isomorphism principle, the observation of critical opalescence is evidence of the existence of the micro-heterogeneous phase. For the ternary mixture of 3MP + water + NaBr, with the presence of the micro-heterogeneous phase at the tri-critical point, then $C = 3$, and $P = 2$, which according to Eq. (2.85) corresponds to $F = 3$, the critical opalescence is expected. The existence of the micro-heterogeneous phase has been confirmed by multiple methods [61,79,82–87] and the convincing photographs has also been reported [82,83]. Therefore, the prediction which is made by the phase rule and isomorphism principal analysis are consistent with our experimental results and the observations of critical opalescence in ternary mixtures.
CHAPTER 6 SUMMARY

The phase rule and isomorphism principal analysis have been applied to the multicomponent system to investigate the critical effects on the solubility and turbidity of multicomponent systems. The Griffiths-Wheeler rule concludes that the critical effect is the divergence of a thermodynamic derivative of a density variable with respect to a field variable and the degree of the divergence depends on the path of approaching the critical point and the number of fixed density variables. If the path of the derivative makes an angle to the coexistence curve in the vicinity of critical point, the derivative (1) diverges strongly with no fixed density variable; (2) diverges weakly with one fixed density variable; (3) remains finite with more than one fixed density variable. To determine the number of intensive variables, the Gibbs phase rule has been modified so it can apply to the intricate system with components that are chemically reactive with respect to each other, which makes the application of the Griffiths-Wheeler rule to predict critical effect in multicomponent systems practical. Additionally, the principle of critical point isomorphism suggests the analysis method applies to all systems in the same universality class.

The regular solution model has been used to describe the liquid mixture system with critical points. Based on the thermodynamic and statistical mechanical analysis, Eq. (3.33) and Eq. (3.50) are derived from the regular solution model to describe the solubility and turbidity in the critical region. We have found that the derivative of the amount of components with respect to the chemical potential, \( \left( \frac{\partial x_i}{\partial \mu_j} \right) \), is the paramount factor in the critical behavior of the solubility and turbidity in liquid mixtures, as shown in Eq. (3.33) and Eq. (3.50). One shall note that the derivatives, \( \left( \frac{\partial \eta}{\partial \Delta G} \right) \) and \( \left( \frac{\partial n_i}{\partial \mu_j} \right) \), in Eq. (3.33)
and Eq. (50), respectively, can be rewritten as \( \sum_i v_i^{-2} (\partial x_i / \partial \mu_i) \) and \( n (\partial x_i / \partial \mu_j) \). According to the Griffiths-Wheeler rule, the quantity \( \phi^x \sim (\partial x_i / \partial \mu_j) \) will be strongly divergent at the critical point because its path makes an angle with the coexistence surface.

The solubility of nine systems has been measured along the critical isopleth in the heterogeneous equilibria involving the dissolution of solids. The temperature range measured extended from the critical temperature to about 10 \( K \) apart from it. According to the Griffiths-Wheeler rule, the derivate \( (\partial \ln s / \partial \Delta G) \), with less than two density variables held fixed, must diverge at the critical point. Because it is the derivative of a density variable with respect to a field variable. Since the van’t Hoff slope, \( (\partial \ln s / \partial (1/T)) \), is governed by \( (\partial \ln s / \partial (1/T)) \) as \( T \to T_c \), it also diverges in the critical region. In the solubility experiments, the temperature and pressure, which are field variables, are fixed and the rest possible fixed variables are mole fractions of components which are density variables. Thus, the van’t Hoff slope is expected to (1) diverge strongly when \( F = 2 \); (2) diverge weakly when \( F = 3 \); (3) remain finite when \( F \geq 4 \). In order to test experimentally the predictive power of phase rule analysis, solvent pairs and solutes with different physical and chemical properties are selected. The fact that the result of each of the solubility experiments is consistent with the prediction indicates the divergence behavior of the corresponding derivative solely depends on the number of fixed density variables.

Because the critical opalescence is associated with the fluctuation of the refractive index, the liquid mixtures are selected over a wide range of refractive indices. The turbidity is proportional to a linear combination of derivatives of the form \( (\partial n_i / \partial \mu_j) \) at the critical point as shown in Eq. (3.50). Like the solubility, the critical effect on turbidites depends upon the number of independent thermodynamic variables. When \( F = 3 \), the isomorphism principle predicts that the turbidity \( \tau^* \) diverges to infinity as \( T \to T_c \) which the critical opalescence is expected. By contrast, the turbidity \( \tau^* \) should remain finite in the
critical region in the case of $F = 4$. The result of our turbidity experiments not only proves these predictions but also can be used to explain the existence of the micro-heterogeneous phase at the tri-critical point of the ternary mixture of 3MP + water + NaBr.

Due to the existence of the critical opalescence, the optical measurement method used to be limited in the critical region of liquid mixtures. However, the phase rule analysis and turbidity measurement of the mixture of EG + 1N suggests that the opalescence can be suppressed by the closely identical refractive indices while the fluctuations still exist in the critical region. Hence, the future work should focus on exploiting a polarized light to probe the mixture of EG + 1N, or other mixtures with closely identical refractive indices, in a search for potential chiral structure in the spatial fluctuations in composition near the critical point.
REFERENCES


Phys. 21, 613 (1920).


[81] M. Bier, J. Mars, H. Li, and M. Mezger, *Salt-Induced Microheterogeneities in Binary Liquid*
