Phase Diagram for Two Completely Miscible Components Systems

Before we discuss the phase diagram for two completely miscible components systems, it is better to recall the Gibbs phase rule which states that

$$F = C - P + 2$$ \hspace{1cm} (110)

Where $F$ is the number of degrees of freedom, $C$ represents the number of components and $P$ simply gives the total number of phases. For a two components system, the equation (110) reduces to

$$F = 2 - P + 2 = 4 - P$$ \hspace{1cm} (111)

At this point, there are three major possibilities depending upon the number of phases involved which will be discussed one by one.

Types of Two-Component Systems Based on Number of Phases

i) When we use $P = 1$ in equation (111), we get

$$F = 4 - 1 = 3$$ \hspace{1cm} (112)

This means that for a one-phase and two-component system, there are three degrees of freedom. This single-phase can be gaseous, solid solution, or two completely miscible liquids. Moreover, since the number of degrees of freedom is three, there are three conditions that can be varied without disturbing the total number of phases at equilibrium state.

Figure 3. The graphical representation of a one-phase, two-component system.

Hence, the three degrees of freedom can be depicted along the three axes of a cube. However, it is more common to vary only two variables while keeping the third one as constant. For instance, in case of pressure-temperature diagrams, composition is kept constant; while in case of pressure-composition curves, the temperature is kept fixed at a particular value. Furthermore, in case of temperature-composition curves, the pressure of the system is always kept constant. Now although all the possibilities are there, it is more convenient to fix the pressure of the system at atmospheric pressure and vary the temperature and composition.
Therefore, we can say that instead of using three variables, it is more popular to keep one constant and vary the other two. This will also simplify the graphical representation of a simple two-component system.

![Figure 4. The two-dimensional variants of the one-phase-two-component system.](image)

\[ F = C - P + 1 \] (115)

Which is the reduced or condensed phase rule where \( F' \) is the total number of degrees of freedom excluding pressure. Now because the total number of phases that can exist simultaneously are reduced to 2 (system become univariant at \( P = 2 \)), The complete phase diagram can be drawn on two dimensional paper with vertical and horizontal sides representing temperature and pressure, respectively.
Types of Completely Miscible Two-Component Systems in Solid-Liquid Equilibria

We know that in a solid-liquid equilibrium, the solid can be one of the constituents or solid solution which are completely miscible in the liquid phase.

Consider a liquid mixture of two components $A$ and $B$ at temperature $T$. Now if this liquid mixture is allowed to cool down below the freezing point of the mixture, the solid will start to separate out. At this point, assume that we have a number of such mixtures with the same components $A$ and $B$ but with different compositions (i.e. with different ratios of $A$ and $B$). The cooling of all the mixtures is carried out in open vessels so that the pressure remains constant (atmospheric pressure). After that, the only thing we need to do is to plot these freezing point vs the composition. These completely miscible two-component systems can primarily be classified into three categories.

1. Eutectic systems: In these types of systems, the components do not react with each other but only the simple mixing takes place in the solution or in the molten state. The common examples of such systems are lead-silver system, bismuth-cadmium system, potassium iodide-water system.

2. Systems forming solid compounds $A_xB_y$ with congruent and incongruent melting points: In these types of systems, the components do react with each other and the formation of a compound takes place. The common example of such systems are the Mn-Zn system (forming MgZn$_2$) and Na$_2$SO$_4$-H$_2$O system (forming Na$_2$SO$_4$.10H$_2$O). These types of systems can further be classified.
   i) Systems forming solid compounds with congruent melting point: In these types of systems, the two components react to give a compound which is quite stable until its melting point is reached. When melted, the composition remains the same as that of the solid, and such compounds are said to have a congruent melting point. Some of the common examples of such systems are Mg-Zn and FeCl$_3$-H$_2$O systems.
ii) Systems forming solid compounds with incongruent melting point: In these types of systems, the two components react to give a compound which is not stable up to its melting point. When heated, the decomposition starts before the melting point is reached; and a new solid phase and a solution or melt with a different composition from the original solid are formed. Such compounds are said to undergo peritectic or transition reaction are labeled to have a congruent melting point. Some of the common examples of such systems are Na$_2$SO$_4$-H$_2$O and NaCl-H$_2$O systems. A typical transition can be represented as

\[ C_1 \rightleftharpoons C_2 + \text{melt or solution} \] (116)

Where $C_1$ is the compound formed by the reaction between participating components whereas $C_2$ represents the compound formed as a result of decomposition of $C_1$ below its fusion temperature.
3. **Systems forming solid solutions**: In these types of systems, the components are completely miscible with each other in solid phase and completely homogeneous solid solutions are produced. The X-ray diffraction studies are typically employed to check that single crystalline phase is obtained rather than a mixture of two solid phases. The common example of such systems are Co-Ni system, Au-Ag system and AgCl-NaCl system.

![Figure 8. The general phase diagram of systems forming solid solutions.](image)

**Experimental Methods for The Determination of Phase Diagram of Two-Component Systems**

The most common approaches for the determination of phase diagram of two-component systems are “cooling curve” and “thaw melt” methods. These methods are quite popular due to their easiness and practicability to many systems.

1. **Cooling curve method**: In this approach, a liquid mixture of two components $A$ and $B$ at temperature $T$ is allowed to cool down below the freezing point of the mixture, the solid will start to separate out. A number of such mixtures with the same components $A$ and $B$ but with different compositions (i.e. with different ratios of $A$ and $B$) are then allowed to cool down in open vessels so that the pressure remains constant (atmospheric pressure). The temperature of the system is regularly recorded at different times to obtain temperature vs time plots. After that, from the breaks and arrests in those plots, important information such as freezing point or solidification time are obtained for different compositions.

Now in order to understand the concept more clearly, a variation of temperature with time for pure and a liquid mixture must be discussed. In the case of a liquid mixture, above point $b$, the system is completely liquid and it will cool down very rapidly in going from point $a$ to point $b$. Now because at point $b$, the crystallization of the compound $A$ will start releasing a large amount of heat, and therefore, the rate of cooling will be slightly slower until point $c$ is reached. Now since the system is getting solidified at eutectic temperature i.e. it is moving from $c$ (solidification of $B$ starts) to $d$ the temperature of the system will remain constant during this conversion. After point $d$, the system will cool down as a solid mixture with two degrees of freedom.
It is also worthy to mention that in some cases a phenomenon called “supercooling” is observed in which the break at point ‘b’ is absent and cooling of liquid continues along a-b with sudden rise after some time giving an abnormal break at b’ instead of b. The correct break is found by extrapolating from point b’ backward.

Figure 9. The typical cooling curves for pure a pure liquid (left) and a liquid mixture (right).

Figure 10. The typical cooling curves for a liquid mixture with supercooling.

Now although the supercooling phenomenon does not create a major problem in most of the cases, it can be a real mess in some systems. Therefore, another method that can overcome these limitations must be discussed.
2. Thaw-melt method: This method is free from the limitation of the “supercooling phenomenon” posed by the cooling curve method. In this approach, a solid mixture of two components $A$ and $B$ at temperature $T$ is heated continuously. This is exactly opposite of what we follow in cooling curve method and we will note down melting points for different compositions. A number of such solid mixtures with same components $A$ and $B$ but with different compositions (i.e. with different ratios of $A$ and $B$) are then heated up in open vessels so that the pressure remains constant (atmospheric pressure). The temperature of system is regularly recorded at different times to obtain temperature vs time plots. After that, from the breaks and arrests in those plots, important information such as melting point or liquefaction time are obtained for different compositions.

Now in order to understand the concept more clearly, a variation of temperature with time for pure and a liquid mixture must be discussed. In the case of a solid mixture, below point $e$, the system is completely solid and it will heat up slowly in going from point $e$ to point $d$. Now since the system is getting liquefied at eutectic temperature i.e. it is moving from $d$ to $c$; the temperature of the system will remain constant during this conversion. Now because at point $e$, the melting of $A$ compound will continue requiring a large amount of heat, and therefore, the rate of heating will be slightly slower until point $b$ is reached. After point $b$, the system will heat up as liquid mixture with two degrees of freedom very rapidly.

Figure 11. The typical Thaw-melting heating curves (temperature vs time) for a pure liquid (left) and a liquid mixture (right).

It is also worthy to mention that the temperature at which the melting of the solid mixture starts is typically called as “thaw point” and the temperate at which liquefaction ends is called as “melting point”.

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**Figure 11.** The typical Thaw-melting heating curves (temperature vs time) for a pure liquid (left) and a liquid mixture (right).
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# Table of Contents

**CHAPTER 1** ................................................................................................................................................ 11

*Quantum Mechanics – I* ................................................................................................................................. 11
  - Postulates of Quantum Mechanics ........................................................................................................ 11
  - Derivation of Schrodinger Wave Equation ......................................................................................... 16
  - Max-Born Interpretation of Wave Functions ..................................................................................... 21
  - The Heisenberg’s Uncertainty Principle .......................................................................................... 24
  - Quantum Mechanical Operators and Their Commutation Relations ................................................. 29
  - Hermitian Operators – Elementary Ideas, Quantum Mechanical Operator for Linear Momentum, Angular Momentum and Energy as Hermitian Operator ......................................................... 52
  - The Average Value of the Square of Hermitian Operators ............................................................ 62
  - Commuting Operators and Uncertainty Principle \((x & p; E & t)\) .................................................... 63
  - Schrodinger Wave Equation for a Particle in One Dimensional Box .............................................. 65
  - Evaluation of Average Position, Average Momentum and Determination of Uncertainty in Position and Momentum and Hence Heisenberg’s Uncertainty Principle .................................................. 70
  - Pictorial Representation of the Wave Equation of a Particle in One Dimensional Box and Its Influence on the Kinetic Energy of the Particle in Each Successive Quantum Level ..................................................... 75
  - Lowest Energy of the Particle ......................................................................................................... 80
  - Problems .......................................................................................................................................... 82
  - Bibliography .................................................................................................................................... 83

**CHAPTER 2** ................................................................................................................................................ 84

*Thermodynamics – I* ......................................................................................................................................... 84
  - Brief Resume of First and Second Law of Thermodynamics .......................................................... 84
  - Entropy Changes in Reversible and Irreversible Processes ............................................................. 87
  - Variation of Entropy with Temperature, Pressure and Volume ...................................................... 92
  - Entropy Concept as a Measure of Unavailable Energy and Criteria for the Spontaneity of Reaction ................................................................................................................................................................. 94
  - Free Energy, Enthalpy Functions and Their Significance, Criteria for Spontaneity of a Process ... 98
  - Partial Molar Quantities (Free Energy, Volume, Heat Concept) ................................................... 104
  - Gibb’s-Duhem Equation ................................................................................................................ 108
  - Problems ........................................................................................................................................ 111
  - Bibliography .................................................................................................................................. 112
CHAPTER 3 .............................................................................................................................................. 113

Chemical Dynamics – I ........................................................................................................................ 113

- Effect of Temperature on Reaction Rates ...................................................................................... 113
- Rate Law for Opposing Reactions of 1st Order and 2nd Order ..................................................... 119
- Rate Law for Consecutive & Parallel Reactions of 1st Order Reactions ....................................... 127
- Collision Theory of Reaction Rates and Its Limitations ............................................................... 135
- Steric Factor ................................................................................................................................... 141
- Activated Complex Theory ........................................................................................................... 143
- Ionic Reactions: Single and Double Sphere Models ..................................................................... 147
- Influence of Solvent and Ionic Strength ........................................................................................ 152
- The Comparison of Collision and Activated Complex Theory ..................................................... 157
- Problems ........................................................................................................................................ 158
- Bibliography .................................................................................................................................. 159

CHAPTER 4 .............................................................................................................................................. 160

Electrochemistry – I: Ion-Ion Interactions .......................................................................................... 160

- The Debye-Huckel Theory of Ion-Ion Interactions ....................................................................... 160
- Potential and Excess Charge Density as a Function of Distance from the Central Ion ................. 168
- Debye-Huckel Reciprocal Length ................................................................................................... 173
- Ionic Cloud and Its Contribution to the Total Potential ................................................................. 176
- Debye-Huckel Limiting Law of Activity Coefficients and Its Limitations ................................... 178
- Ion-Size Effect on Potential ........................................................................................................... 185
- Ion-Size Parameter and the Theoretical Mean - Activity Coefficient in the Case of Ionic Clouds with Finite-Sized Ions................................................................................................................................. 187
- Debye-Huckel-Onsager Treatment for Aqueous Solutions and Its Limitations ............................ 190
- Debye-Huckel-Onsager Theory for Non-Aqueous Solutions ........................................................ 195
- The Solvent Effect on the Mobility at Infinite Dilution ................................................................ 196
- Equivalent Conductivity ($\lambda$) vs Concentration $C^{1/2}$ as a Function of the Solvent .............. 198
- Effect of Ion Association Upon Conductivity (Debye-Huckel-Bjerrum Equation) ..................... 200
- Problems ........................................................................................................................................ 209
- Bibliography .................................................................................................................................. 210

CHAPTER 5 .............................................................................................................................................. 211

Quantum Mechanics – II .................................................................................................................. 211

- Schrodinger Wave Equation for a Particle in a Three Dimensional Box ..................................... 211
The Concept of Degeneracy Among Energy Levels for a Particle in Three Dimensional Box 215

Schrodinger Wave Equation for a Linear Harmonic Oscillator & Its Solution by Polynomial Method 217

Zero Point Energy of a Particle Possessing Harmonic Motion and Its Consequence 229

Schrodinger Wave Equation for Three Dimensional Rigid Rotator 231

Energy of Rigid Rotator 241

Space Quantization 243

Schrodinger Wave Equation for Hydrogen Atom: Separation of Variable in Polar Spherical Coordinates and Its Solution 247

Principal, Azimuthal and Magnetic Quantum Numbers and the Magnitude of Their Values 268

Probability Distribution Function 276

Radial Distribution Function 278

Shape of Atomic Orbitals (s, p & d) 281

Problems 287

Bibliography 288

CHAPTER 6 289

Thermodynamics – II 289

Clausius-Clapeyron Equation 289

Law of Mass Action and Its Thermodynamic Derivation 293


Phase Diagram for Two Completely Miscible Components Systems 304

Eutectic Systems (Calculation of Eutectic Point) 311

Systems Forming Solid Compounds AₓBᵧ with Congruent and Incongruent Melting Points 321

Phase Diagram and Thermodynamic Treatment of Solid Solutions 332

Problems 342

Bibliography 343

CHAPTER 7 344

Chemical Dynamics – II 344

Chain Reactions: Hydrogen-Bromine Reaction, Pyrolysis of Acetaldehyde, Decomposition of Ethane 344

Photochemical Reactions (Hydrogen-Bromine & Hydrogen-Chlorine Reactions) 352

General Treatment of Chain Reactions (Ortho-Para Hydrogen Conversion and Hydrogen-Bromine Reactions) 358
<table>
<thead>
<tr>
<th>Chapter 8: Electrochemistry – II: Ion Transport in Solutions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Apparent Activation Energy of Chain Reactions: 362</td>
</tr>
<tr>
<td>Chain Length: 364</td>
</tr>
<tr>
<td>Rice-Herzfeld Mechanism of Organic Molecules Decomposition (Acetaldehyde): 366</td>
</tr>
<tr>
<td>Branching Chain Reactions and Explosions (H₂-O₂ Reaction): 368</td>
</tr>
<tr>
<td>Kinetics of (One Intermediate) Enzymatic Reaction: Michaelis-Menten Treatment: 371</td>
</tr>
<tr>
<td>Evaluation of Michaelis's Constant for Enzyme-Substrate Binding by Lineweaver-Burk Plot and Eadie-Hofstee Methods: 375</td>
</tr>
<tr>
<td>Competitive and Non-Competitive Inhibition: 378</td>
</tr>
<tr>
<td>Problems: 388</td>
</tr>
<tr>
<td>Bibliography: 389</td>
</tr>
</tbody>
</table>

**INDEX** 427
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