NOTES ON DIFFERENTIAL THERMAL ANALYSIS

BACKGROUND ON PHASE EQUILIBRIA

Phase diagrams as a complete physical description of the system at equilibrium in terms of intensive properties of the system (p, T, or composition if multiple components).

(1) For pure substance

Phase rule – With the number of components and phases specified, the number of degrees of freedom (how many intensive properties can be INDEPENDENTLY varied) is specified:

\[ F = C - P + 2 \]

- \( C \) = # components
- \( P \) = # phases
- \( F \) = # degrees of freedom (number of variables that can be independently varied without altering the numbers or kinds of phases)

e.g. for 1 phase of a pure substance, need T and p (\( F = 2 \)), if 2 phases present, only either T or p can be independently varied.

The relationship between T and p of a pure substance during a phase change is given by:
Clapeyron eqn.: \[
\frac{dp}{dT} = \frac{\Delta H_{\text{vap,fus}}}{T \Delta V_{\text{vap,fus}}} \quad \text{and, after integrating:}
\]
\[
p = p' + \frac{\Delta H_{\text{fus}}}{\Delta V_{\text{fus}}} \ln \left( \frac{T}{T'} \right)
\]

(2) For a 2-component system (A and B)

(a) 1 phase is present \((F = 3)\), need 3 independent coordinates to specify the state of the system (e.g. a point on a 3D graph with \(T\), \(p\), and \(x_B\) as the axes).

(b) 2 phases present \((F = 2)\)

  e.g. L and V at equilibrium (binary liquid-vapor phase diagram). If \(T\) and \(p\) are specified, \(x_{BL}\) and \(x_{BV}\) (the composition of the liquid and vapor) are fixed \((\text{see Figures 1-3 on pgs. 209–211})\)

At a specific pressure (cross-section of a 3D plot):

The vapor pressure of each component (A) and (B) vary with their mole fraction according to Henry’s Law:
Consider binary mixtures of two solids (A) and (B). Equilibria are easier since the changes are essentially independent of pressure changes of a few atmospheres (small change in molar volume). The solids can be:

- Pure A
- Pure B
- Liquid (A..B) (L)
- “solutions” of solid A in solid B (β) (crystals interdispersed in each other)
- “solutions” of solid B in solid A (α)

If solid A and solid B do not have compatible lattice structure, they are “immiscible” in each other and α reduces to pure A and β to pure B:
See text and handout … can show that the “solid-liquid” or “liquidus” curve is given by:

(i) \[ T = T_A + \frac{RT_A^2}{\Delta H_{fus}} \ln \chi_A \] where \( \chi_A = 1 - \chi_B \) and \( T_A \) is the m.p. of A

(ii) \[ T = T_B + \frac{RT_B^2}{\Delta H_{fus}} \ln \chi_B \]

TO DO:

(1) Obtain measurements of the phase change (e.g. melting) temperature (T) vs. \( \chi_B \). Plot as points

(2) The enthalpy of fusion can be estimated from tangential lines of a T vs. \( \ln \chi_B \) plot (e.g. construct T vs. \( \ln \chi_B \) plot)

(3) With a knowledge of the enthalpy of fusion, the T vs. mole fraction curve can be calculated and plotted (you will do as “theoretical” liquidus curve).
(4) You will compare these two curves, as well as your enthalpies of fusion to those from reference books.

(5) The composition at which the melting temperature (T at S-L interface) of “A” solution = the melting temperature of “B” solution a “eutectic” is formed (phase boundary between solid A+B and liquid).

The data:

Consider “cooling” different mixtures of A and B and what the T vs. time plots would look like (Figure 2 on pg. 217).

Points:

1. In the first curve (I), a rapid cooling takes place until the phase boundary is reached.

2. At that time, there is no change in temperature while the “pure” sample crystallizes.

3. This is also observed in curve (III) at the eutectic composition.

4. In curve (II), the rate of cooling is slowed as A crystallizes out.

The experiment: Map the ΔT associated with the phase transition (as a function of the composition):
When a sample melts, heat is consumed (endothermic):

\[ s + \Delta \rightarrow L \]

When a sample crystallizes, heat is evolved (exothermic):

\[ L \rightarrow s + \Delta \]

If, as a function of temperature, we can measure when an endothermic or exothermic phase transition occurs, we can “map out” the phase diagram:

What would the T vs. time profiles look like at various compositions? (Figure 2 on pg. 217)

The temperature change will be small … how do we measure it?

Differential Thermal Analysis Experiment.

Objective: For given binary compositions, “map” temperatures at which phase boundaries occur to obtain the binary phase diagram.
How:

(1) A “reference” material and sample (of known composition) are simultaneously heated.
(2) The reference (Al₂O₃) has no phase transitions within the heating range and is heated linearly:

(3) The sample is simultaneously heated. When a phase transition occurs, heat is either consumed (melting) or given to the surroundings (crystallization). The temperature deviates from that of the reference.

(4) If the sample is pure, the melting and crystallization times will be “sharp.” If the sample is a mixture, the “transition” time will be diffuse.
The $\Delta T$ defines the boundaries of the phase transition region.

The apparatus:

The voltage drop across a thermocouple is proportional to the temperature.

The DIFFERENTIAL voltage between the sample and reference is measured using two differential inputs of an A/D board as follows:

Channel 1: Differential voltage between reference and sample ($V_{\text{ref}} - V_{\text{sam}}$).
Channel 0: Differential voltage between sample and ice (allows an absolute determination of temperature) \((V_{\text{ice}} - V_{\text{sam}})\).

Data (a): Channel 0 \((T_{\text{sam}})\) vs. heating time

However, the \(\Delta T\) is small compared to \(T\) … Plot differential \(T\) vs. \(T_{\text{ref}}\):

As a function of composition to map out phase diagram.