

Binary Solid-Liquid Phase Diagram

Introduction

The substances that we encounter in the material world are hardly ever pure chemical compounds but rather mixtures of two or more such compounds. The individual substances in such a mixture may behave more or less independent of each other but merely diluted, *i.e.*, an ideal solution or mixture, or there may be substantial chemical interaction or complex formation between the constituents. The study of such mixtures can lead to an understanding of the most fundamental intermolecular interactions.

In the present experiment, the phase changes that occur in a two-component mixture will be investigated. The three common phases of matter are the solid, liquid and vapor states. The particular phase or phases in which a pure substance or mixture exists under a given set of conditions, *e.g.*, temperature, pressure and composition, is obviously of utmost importance in our use of or interaction with the myriad of material substances in the world. We take it for granted that the mixtures air, ocean water and wood exist in the vapor, liquid and solid states at ambient conditions. In the preparation of countless commercial chemical products, great effort is taken to insure that the final product, usually a complex mixture, is in an attractive and practical physical state. Solid toothpaste and liquid margarine would not sell!

While you may never have thought about it, when salt water freezes, as it must if the temperature is sufficiently low, the solid substance is pure water with no NaCl or other dissolved solutes incorporated into the ice lattice. The present experiment assumes in the first place that when solid precipitates from a liquid *mixture* on cooling, the solid is a pure substance in equilibrium with the remaining liquid solution. In the salt water analogy, the solid ice (pure H₂O) is in equilibrium with the liquid H₂O that remains in the unfrozen salt water.

Mixtures of naphthalene and diphenylamine, both solids in the pure state at room temperature, will be prepared and their phase transitions studied by means of a thermal analysis. The details of this experiment are provided in Reference 1.

Secondly, the assumptions used in going from the Clapeyron equation

$$\frac{dP}{dT} = \frac{\Delta H}{T\Delta V} \quad (1)$$

relating the change in vapor pressure with temperature to the enthalpy and volume changes to the integrated form of the Clausius-Clapeyron equation

$$\ln \frac{P_1}{P_0} = \frac{\Delta_{\text{vap}}H}{R} \left(\frac{1}{T_0} - \frac{1}{T_1} \right) \quad (2)$$

are taken to be valid. In equation (2), $\Delta_{\text{vap}}H$ is the enthalpy of vaporization of pure solvent which has vapor pressures P_0 at T_0 , and P_1 at T_1 . These assumptions are that the vapor behaves as an ideal gas, the volume of the condensed phase is negligible in contrast to the volume of the vapor and finally, that the enthalpy change accompanying vaporization is independent of temperature.

Finally, it is assumed that Raoult's Law is obeyed, namely that in a mixture, the vapor pressure of one component, P_1 is directly proportional to the mole fraction of that component in the mixture, X_1 , and to the vapor pressure of the pure component, P_1^0

$$P_1 = X_1 P_1^0 \quad (3)$$

where

$$X_1 + X_2 = 1 \quad (4)$$

for a two component systems.

Let us consider the situation of our mixtures of diphenylamine (A) and naphthalene (B). There are four possible combinations, neglecting the vapors of the two substances, a reasonable assumption at temperatures just above their melting points. We can have

- I) liquid A mixed homogeneously with liquid B.
- II) solid A in heterogeneous equilibrium with the solution.
- III) solid B in heterogeneous equilibrium with the solution.
- IV) solid A mixed with solid B.

It is interesting to note that II (and, in a reciprocal manner, III) can be viewed in either of two ways. The appearance of solid A in II will begin to occur at a lower temperature than will solid A begin to occur in pure melted A. This is an illustration of the *freezing point* (solidification) *lowering* of A as the result of the presence of some B in mixture II. Alternatively, mixture II can be viewed as representing the maximum *solubility*, at the given temperature, of component A in component B.

At the freezing point of this mixture, solid A and liquid A are in equilibrium and, therefore, the chemical potentials, μ , or the molar Gibbs free energies, \bar{G} , must be equal (definition of equilibrium) for A (solid) and A (solution)

$$\mu_A^0(\text{solid}) = \mu_A(\text{solution}) = \mu_A^0(\text{liquid}) + RT \ln(\gamma_A X_A) \quad (5)$$

or

$$\bar{G}_A^0(\text{solid}) = \bar{G}_A(\text{solution}) = \bar{G}_A^0(\text{liquid}) + RT \ln(\gamma_A X_A) \quad (6)$$

where γ_A is the mole-fraction-scale activity coefficient that, on the assumption of ideal behavior, may be set equal to unity. The standard molar free energy of fusion would be

$$\Delta_{fus} \bar{G}_A^0 = \bar{G}_A^0(\text{liquid}) - \bar{G}_A^0(\text{solid}) \quad (7)$$

Remembering that in general

$$\Delta G = \Delta H - T \Delta S \quad (8)$$

or

$$\frac{\Delta G}{T} = \frac{\Delta H}{T} - \Delta S \quad (9)$$

which leads to the Gibbs-Helmholtz equation

$$\left[\partial \left(\frac{\Delta G}{T} \right) / \partial T \right]_P = - \frac{\Delta H}{T^2} \quad (10)$$

Combination^{1,2,3} of equations (2), (3), (6), (7) and (10) leads to the equation

$$T \cong T_A + \frac{RT_A^2}{\Delta H_A} \ln X_A \quad (11)$$

or

$$T \cong T_A + \frac{RT_A^2}{\Delta H_A} \ln(1 - X_B) \quad (12)$$

or

$$T \cong T_A - \frac{RT_A^2}{\Delta H_A} \ln X_B \quad (13a)$$

$$T \cong T_B - \frac{RT_B^2}{\Delta H_B} \ln X_A \quad (13b)$$

where T and T_A are freezing points (K) of the mixture and pure A, R is 8.314 J/K mole, ΔH_A is the molar enthalpy of fusion of A and X_B is the mole fraction of component B in the mixture.

Finally, the Gibbs phase rule will be noted:

$$F = C - P + 2 \quad (14)$$

where for a mixture of C chemical constituents and P "physically differentiable"¹ phases in equilibrium, there will be F degrees of freedom or intensive variables (T , P , *composition*) pertaining to the system that can be varied independently at the equilibrium without altering the number of phases present. This fundamental equation will be illustrated with reference to the phase diagram shown below.

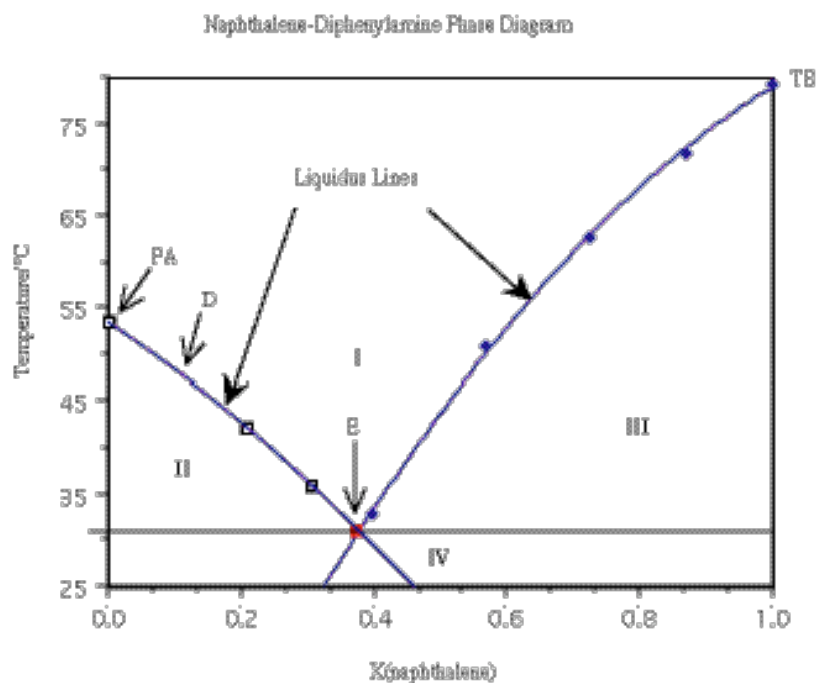


Fig 1.- Phase diagram of the naphthalene-diphenylamine mixture. Data taken by D. Carin '90.

Review the composition of the mixtures I-IV and study this diagram to be certain you understand what is present in the different regions.

Application of equation (14) would give

Point	C	P	F	variable
P_A	1	2	1	pressure
D	2	2	2	pressure and temperature or pressure and composition
E	2	3	1	pressure

Point E is referred to as a eutectic point with a characteristic temperature T_{E} , and mole fraction $X_{B,E}$.

Procedure

Follow pp. 243-245 in Reference 1 (pp. 219-221 in 6th edition). The reading of the electronic thermometer is transferred to the computer and continuously read by a data acquisition card running under a LabVIEW VI. To run the software start LabVIEW and open the file "Temperature Curve" in the Chem 366 folder. Click the hallow arrow button in the top left to start the data acquisition, and use the large "Stop" button on the front panel (see Fig. 2) to end the data acquisition once you notice a break or arrest in the cooling profile. Do not use the little stop-sign button which appears next to the start button once the VI runs (if you do, your data will

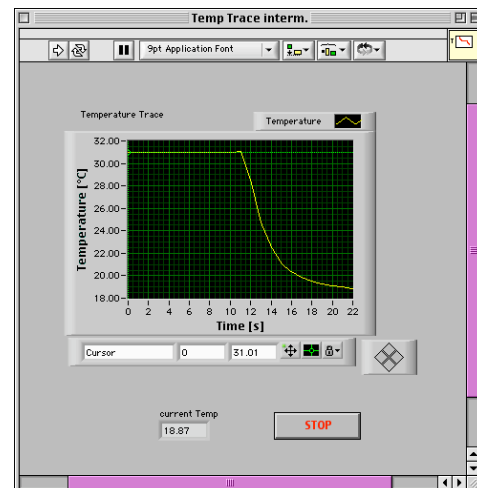


Fig. 2: Front Panel

not be saved, but you can still read the break temperature off of the plot using the cursor below). Upon quitting, the VI asks you for a filename to save your data under. The file dialog is slightly counter-intuitive: Click "New..." and enter your file name in the input field which opens up (see Fig. 3) and click "File"



Fig 3: Save File Dialog

Typical data are shown below (Fig. 4). For a pure substance, usually an "arrest temperature" is noted where the temperature remains constant on freezing (trace I). For a mixture, there will be a brief diminution in the temperature drop, or a "break temperature." As one component *in the mixture* freezes out, the remaining solution becomes richer in the other component and the freezing point continues to drop (Trace II). This does not occur in a pure substance. Remember that in both cases, the temperature drop is slowed because of the release of the enthalpy of solidification to the surroundings. Melting is endothermic, solidification is exothermic.

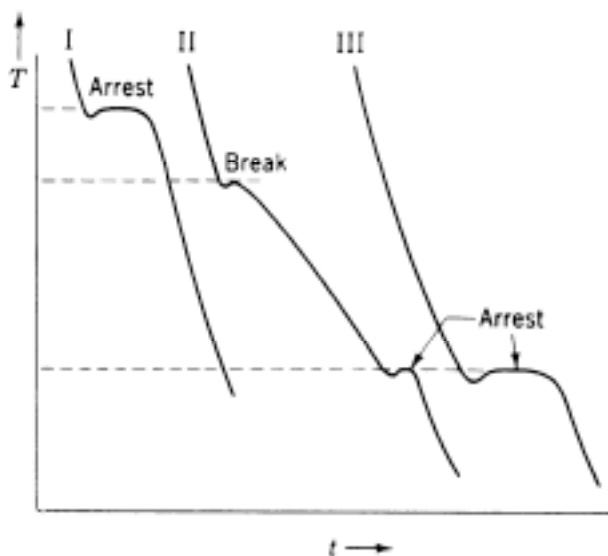


Fig. 4. Sample cooling curves for binary mixtures.
I: pure substance, II: mixture, III: eutectic mixture

Suggested Compositions For Thermal Analysis¹

(A = D = diphenylamine; B = N = Nap = naphthalene)

Run No	Wt.% B	Prepare by adding...	...to sample used in run no.
1	100	5g	B = N
2	83.3	1g	A = D
3	66.7	1.5g	A = D
4	50.0	2.5g	A = D
5	33.3	5g	A = D
6	0	5g	A = D
7	16.7	1g	B = N
8	25.0	0.67g	B = N
9	Eutectic	(see text)	

1. Use weighing paper on the top loading balance and weigh to the nearest 0.01 g. This is a long experiment, so the first person to arrive in lab should start weighing out the samples without waiting for their lab partner.
2. Data must be plotted *in lab* so that a eutectic composition may be prepared for the last run. This is done most readily using Kaleidagraph or Excel software on a Macintosh computer during the experiment.
3. The temperature is measured with an electronic digital thermometer. Try to avoid melting the insulation on the lead to the probe (any further)
4. Discontinue cooling on all runs after the first definite break has occurred.
5. Maintain a well-packed ice-water bath around the cooling tube.
6. Use care to avoid losing any material in making supplemental additions of reagents to the test tube.
7. Planned efficiency is required to complete this experiment during the allotted time.
8. Wearing gloves and working in a hood, use acetone to rinse out the tubes into the waste bottle provided.

Calculations

Convert the weight data (include in your report) to mole fractions. Plot your temperature versus time data and determine the break and arrest temperatures. Plot these temperatures against $X_{B=N}$ and draw the eutectic line and the two liquidus lines.

Equation 13a gives a linear function for the dependence of the freezing point on the mole fraction, X_B , assuming ideal behavior, in the *limit* of $X_B \rightarrow 0$. The slope of the plot T vs X_B in this limit is $-RT_A^2/\Delta\bar{H}_A$ where $\Delta\bar{H}_A$ is the molar enthalpy of fusion of component A. This slope can be determined from the T and X_B values for pure A and for the first mixture containing the least amount of B, using $\Delta T/\Delta X_B$.

Equation 13b gives the same limiting relationship for the region of nearly pure B, where $X_A \rightarrow 0$. The slope of the plot T vs X_A , $-RT_B^2/\Delta\bar{H}_B$, can be determined from the T and X_A values for pure B and for the first mixture containing the least amount of A, using $\Delta T/\Delta X_A$.

Compare your values of $T_{A=D}$, $T_{B=N}$ (the freezing points of the pure components), $\Delta\bar{H}_{A=D}$ and $\Delta\bar{H}_{B=N}$ with appropriate literature values.

Using your observed values of $T_{A=D}$, $T_{B=N}$, $\Delta\bar{H}_{A=D}$ and $\Delta\bar{H}_{B=N}$, plot ideal liquidus lines of T versus $X_{B=N}$ using equations 13a and 13b. Compare the calculated ideal intersection temperature and composition with the eutectic temperature and composition found by experiment.

Report

Include the data (in graphical form--raw numbers are not needed), calculated results, and analysis graphs noted in the Calculations section above.

References

1. D. P. Shoemaker, C. W. Garland, and J. W. Nibler, *Experiments in Physical Chemistry*, 5th Edition, McGraw-Hill, New York, 1994, pp. 195-197, 238-246. (6th edition, pp 179-182, 215-222.)
2. G. P. Matthews, *Experimental Physical Chemistry*, Clarendon Press, Oxford, 1985, pp. 46-48, 52-53.
3. P. P. Blanchette, *J. Chem. Ed.*, **64**, 267-269, 1987.

Safety Notes

Diphenylamine: Potential Health Effects

Eye:

Causes eye irritation.

Skin:

Causes skin irritation. May cause skin sensitization, an allergic reaction, which becomes evident upon re-exposure to this material.

Ingestion:

May cause gastrointestinal irritation with nausea, vomiting and diarrhea.

Inhalation:

May cause respiratory tract irritation.

Chronic:

Prolonged or repeated exposure may cause adverse reproductive effects.

Napthalene

Health Rating: 1 – Slight

Flammability Rating: 2 – Moderate

Reactivity Rating: 0 – None

Contact Rating: 1 – Slight

Lab Protective Equipment: Goggles & Lab Coat

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