Phase Equilibrium: Preliminaries

Phase diagrams for two one component systems, CO₂ and H₂O, are shown below.

The main items to note are the following:

- The lines represent equilibria between two phases.
- The regions “interior” to these lines represent regions where only one phase is present.
- The triple point is a unique, invariant point for each system where three phases are simultaneously in equilibrium.

Thermodynamic condition for equilibrium between two phases \(a\) and \(b\) is \(G_a = G_b\), so that during an equilibrium phase change, \(\Delta G_{ab} = G_a - G_b = 0\).

Note that the slope of the line separating the solid from the liquid region for CO₂ has a positive slope. This is typical of most substances and is indicative of the fact that the solid is denser than the liquid (how?).

On the other hand, the slope of the solid-liquid boundary for water is negative, indicating that the liquid is denser than the solid. This is by far the exception.
The Clapeyron Equation

If we confine ourselves to conditions where two phases, say vapor and liquid, are in equilibrium, we effectively limit ourselves to a one-dimensional world defined by the line separating the liquid region from the vapor region. Under those conditions, the Maxwell relation

$$\left( \frac{\partial p}{\partial T} \right)_V = \left( \frac{\partial S}{\partial V} \right)_T,$$

can be modified as follows:

$$\frac{dp}{dT} \approx \frac{dS}{dV} \approx \frac{S_{m,v} - S_{m,l}}{V_{m,v} - V_{m,l}} = \frac{\Delta_{vap} S_m}{\Delta_{vap} V_m}.$$  

Substituting the definition of entropy change for a phase change, we obtain

$$\frac{dp}{dT} = \frac{\Delta_{vap} H_m}{T \Delta_{vap} V_m}.$$  (1)

This is called the Clapeyron equation.

Similar equations can be written for the solid-vapor boundary (enthalpy of sublimation!) and the solid-liquid boundary (enthalpy of fusion!). Note that, since enthalpy is a state function,

$$\Delta_{sub} H_m = \Delta_{fus} H_m + \Delta_{vap} H_m.$$  

The Clausius-Clapeyron Equation:

Eq. (1) may be written as

$$\frac{dp}{dT} = \frac{\Delta_{vap} H_m}{T \left( V_{m,g} - V_{m,l} \right)} \approx \frac{\Delta_{vap} H_m}{TV_{m,g}} \approx \frac{\Delta_{vap} H_m}{RT^2} P,$$  (2)

where we have assumed that the vapor behaves ideally to get the last equality. This equation may be rearranged and integrated to give

$$\ln(p/\text{units}) = -\frac{\Delta_{vap} H}{RT} + A.$$  (3)

or

$$\ln\left( \frac{p_2}{p_1} \right) = \frac{\Delta_{vap} H_m}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right).$$  (4)

The Clausius-Clapeyron equation is applicable to solid-vapor equilibrium as well. The pressure plotted in the phase diagrams and used in these relationships is the vapor pressure of the substance under consideration, not the total pressure. These equations could give the $P-T$ relationship required to plot the lines in the phase diagrams. Therefore, Eq. (3) for the liquid-vapor and the solid-vapor equilibria can be used to find the triple point for a one-component system.
More sophisticated treatments

Obtaining the integrated form of the Clausius-Clapeyron equation involves three assumptions: (a) the condensed phase volume can be neglected compared to the vapor phase, (b) the vapor behaves ideally, and (c) the enthalpy is independent of temperature. More sophisticated treatments attempt to avoid at least the last assumption by assuming that

\[ \Delta_{\text{vap}}H = B + CT + DT^2 + \ldots \]

which, when substituted in Eq. (2), leads to the integrated equation

\[ \ln p = A - \frac{B}{RT} + \frac{C}{R} \ln T + \frac{D}{R} T + \ldots \]

instead of Eq. (3), where \( A \) is the constant of integration. Another equation, which has proved to be highly successful, is the Antoine equation,

\[ \ln \frac{p}{\text{torr}} = a - \frac{\beta}{T(C) + \gamma}, \]  \hspace{1cm} (5)

where the constants are usually tabulated in standard references for most liquids.

**The Gibbs Equation:**

By definition,

\[ dG = Vdp - SdT. \]

At constant temperature, the second term vanishes and we get

\[ dG = Vdp. \]

For the liquid vapor equilibrium considered earlier, under these circumstances, we have

\[ dG_{m,v} = dG_{m,l} \]

or

\[ V_{m,v}dp = V_{m,l}dP, \]

where the pressure term on the vapor side is the vapor pressure of the substance while on the liquid side, it is the total pressure acting on the liquid surface. Now, using ideal gas law for the vapor, we get
\[
\frac{RT}{p} dp = V_{m,l} dP, \quad \text{or} \\
\frac{dp}{p} = \frac{V_{m,l}}{RT} dP_t,
\]

Now consider a situation where, initially, the total pressure acting on a liquid surface is the total pressure. Let us denote this pressure by \(p_v\). The pressure is then changed by the addition of an inert gas, keeping the temperature fixed, to get a final total pressure \(P_t\). We wish to find the new value of the equilibrium vapor pressure \(p\). For this situation, we may integrate this equation above to get

\[
\ln\left(\frac{p}{p_v}\right) = \frac{V_{m,l}}{RT}(P_t - P_v),
\]

where we have assumed that the liquid volume does not change with applied pressure.

This is called the **Gibbs Equation**.
**Ideal Solutions: Raoult’s Law:**

Consider a solution formed by two miscible liquids A and B. An ideal solution is one for which

- \( V_{\text{soln}} = V_A + V_B \).
- \( \Delta H_{\text{soln}} = 0. \)
- \( \Delta S_{m,\text{soln}} = -R(x_A \ln x_A + x_B \ln x_B). \)
- \( \Delta G_{m,\text{soln}} = RT(x_A \ln x_A + x_B \ln x_B). \)

Ideal solutions obey Raoult’s law exactly. To state Raoult’s law, let us denote the mole fractions in the liquid phase by \( x \) and the mole fractions in the vapor phase by \( y \). Also, we denote the vapor pressure of pure A as \( P_A^* \) and that of B as \( P_B^* \). Raoult’s law can now be written as

\[
p_A = x_A P_A^* \quad \text{and} \quad P_B = x_B P_B^*.
\]

In other words, the partial pressure of a substance in the vapor phase is determined by its mole fraction in the liquid phase. Compare this to the Dalton’s law of partial pressures, which states

\[
p_A = y_A P \quad \text{and} \quad p_B = y_B P,
\]

where the total pressure is denoted as \( P \). If only A and B are present in the gas phase above the solution, we have

\[
P = x_A P_A^* + x_B P_B^*.
\]

Since A and B are the only substances present in solution, we may re-write this as

\[
P = x_A P_A^* + (1 - x_A) P_B^*,
\]

which gives the variation of total pressure as a function of \( x_A \).
Henry’s Law:

Henry’s Law may be written in terms of molality, molarity or mole fractions as

\[ p_B = k_B m_B \approx k_B'' c_B \approx k_B' x_B. \]

In the limit of infinite dilution, solvents usually follow Raoult’s law and solutes usually follow Henry’s law.

The form of Henry’s law preferred by most workers is

\[ p_B = k_B' x_B, \]

where B refers to the component present in small amounts in the solution.

One place where Henry’s law finds useful application is in estimating the concentration of gases dissolved in a solution at a given partial pressure of the gas.

Example:

The total pressure above the solution is 750 torr, which consists of the partial pressure of methane and benzene. In other words,

\[ P = p_{CH_4} + p_{Bz}. \]

This question actually presents a “catch-22” situation. We have no way of calculating the actual partial pressure of benzene, \( p_{Bz} \) (for which we would use Raoult’s law since benzene is present in large quantities and can be considered the solvent), without knowing the mole fraction of benzene in the solution, \( x_{Bz} \), which we cannot know until we find the mole fraction of methane in solution. But the whole purpose of the question is to find the mole fraction of methane in solution!

So, since methane obviously cannot have a high concentration, we assume that \( x_{Bz} \approx 1 \) and, therefore, \( p_{Bz} \approx p_{Bz^*} \). Then we have

\[ p_{CH_4} = P - p_{Bz}^{*} = 750 - 94.6 = 655.4 \text{ torr} \]

Now we can use Henry’s law for methane to get

\[ p_{CH_4} = k_{CH_4}' x_{CH_4}, \]

and solve for the mole fraction of methane.

We should verify that this indeed is a small number so that the assumption made regarding the partial pressure of benzene is valid.
Non-ideal solutions:

Non-ideal solutions are those that deviate from Raoult’s law.

Positive deviation from Raoult’s law:

\[ P > x_A p_A^* + (1 - x_A) p_B^*. \]

Negative deviation from Raoult’s law:

\[ P < x_A p_A^* + (1 - x_A) p_B^*. \]

In many solutions, both components show the same type of deviation (positive or negative) from Raoult’s law so that we have either

\[ p_A > x_A p_A^* \text{ and } p_B > x_B p_B^* \]

or

\[ p_A < x_A p_A^* \text{ and } p_B < x_B p_B^*. \]

However, there are exceptions to this behavior.
Raoult’s Law and Activities

Consider a binary system consisting of a solution and a vapor phase, each containing components A and B. The equilibrium condition is:

\[ G_A^{\text{sol}} = G_A^{\text{vap}} \quad \text{or} \quad \mu_A^{\text{sol}} = \mu_A^{\text{vap}} \quad \text{and} \quad G_B^{\text{sol}} = G_B^{\text{vap}} \quad \text{or} \quad \mu_B^{\text{sol}} = \mu_B^{\text{vap}}. \]

If the vapor phase behaves ideally, we may write (with \( p^o = \) standard pressure)

\[ G_A^{\text{vap}} = G_A^{\text{vap}} + n_A RT \ln \left( \frac{p_A}{p^o} \right), \quad \text{and} \quad G_B^{\text{vap}} = G_B^{\text{vap}} + n_B RT \ln \left( \frac{p_B}{p^o} \right) \]

Now, at equilibrium, we may write

\[ G_A^{\text{sol}} = G_A^{\text{vap}} + n_A RT \ln \left( \frac{p_A}{p^o} \right), \quad \text{and} \quad G_B^{\text{sol}} = G_B^{\text{vap}} + n_B RT \ln \left( \frac{p_B}{p^o} \right), \]

or

\[ \mu_A^{\text{sol}} = \mu_A^{\text{vap}} + RT \ln \left( \frac{p_A}{p^o} \right) \quad \text{and} \quad \mu_B^{\text{sol}} = \mu_B^{\text{vap}} + RT \ln \left( \frac{p_B}{p^o} \right) \]

For the pure liquids in equilibrium with their vapors, we write

\[ \mu_A^{\text{sol}} = \mu_A^{\text{vap}} + RT \ln \left( \frac{p_A}{p^o} \right) \quad \text{and} \quad \mu_B^{\text{sol}} = \mu_B^{\text{vap}} + RT \ln \left( \frac{p_B}{p^o} \right) \]

From the last two equations, we write (all equations written for component A can also be written for B):

\[ \mu_A^{\text{sol}} = \mu_A^{\text{sol}} - \mu_A^{\text{vap}} = RT \ln \left( \frac{p_A}{p^o} \right) - RT \ln \left( \frac{p_A}{p^o} \right), \quad \text{or} \]

\[ \mu_A^{\text{sol}} = \mu_A^{\text{sol}} + RT \ln \left( \frac{p_A}{p^o} \right) \]

If the solution behaves ideally (i.e., obeys Raoult’s law), then \( p_A/p_A^* = x_A \). Therefore, we get

\[ \mu_A^{\text{sol}} = \mu_A^* + RT \ln x_A \]

For non-ideal solutions, the ratio \( p_A/p_A^* \) is called the activity of A, \( a_A \). In this case, we write

\[ \mu_A^{\text{sol}} = \mu_A^* + RT \ln a_A \]

As \( p_A \) approaches \( p_A^* \), it is clear that the activity approaches unity. This is the basis for assigning the value of 1 to the activities of all pure substances.
Colligative Properties

Let us consider the consequence of dissolving a nonvolatile solute $B$ in a solvent $A$. Since the solute cannot be present in the vapor phase, this immediately leads to a lowering of vapor pressure, because $x_A < 1$ and, therefore, $p_A = x_A p_A^* < p_A^*$. This lowering of vapor pressure is responsible for both lowering the freezing point as well as raising the boiling point of the solvent.

Freezing Point Depression:

For the equilibrium between the liquid and solid phases, we require $\mu^l_A = \mu^s_A$, or $\mu^s_A + RT \ln x_A = \mu^l_A$, from which we get

$$\ln x_A = \frac{\mu^s_A - \mu^s_A}{RT} = -\frac{\Delta_{fus} G_{A,m}}{RT}, \text{ at constant } T \text{ and } P.$$  

Differentiating both sides with respect to $T$, we get

$$\frac{d \ln x_A}{dT} = -\frac{1}{R} \left[ \frac{\partial (\Delta_{fus} G_{A,m}/T)}{\partial T} \right] = -\frac{\Delta_{fus} H_m}{RT^2}, \text{ at the equilibrium temperature.}$$

Now we rearrange and integrate both sides, the LHS from a mole fraction of $x_A = 1$ (pure solvent) to the solvent mole fraction in solution, $x_A < 1$, and correspondingly, the RHS from a liquid-solid equilibrium temperature of $T^*_f$ (freezing point of the pure solvent) to $T$, the freezing point of the solution. This yields

$$\ln x_A = \frac{\Delta_{fus} H_m}{R} \left( \frac{1}{T^*_f} - \frac{1}{T} \right). \quad (6)$$

We may re-write this as

$$\ln(1 - x_B) = \frac{\Delta_{fus} H_m}{R} \left( \frac{T - T^*_f}{T^*_f T} \right). \quad (7)$$

We now make two simplifications: for small $x_B$, $\ln(1-x_B) \approx -x_B$ and $T^*_f T_f \approx T^*_f^2$. This gives

$$x_B = \frac{\Delta_{fus} H_m}{R} \left( \frac{\Delta T_f}{T^*_f^2} \right),$$

which can be further simplified to yield

$$\Delta T_f = \frac{RT^*_f^2 M_A}{\Delta_{fus} H_m} m_B \text{ or } \Delta T_f = K_f m_B, \quad (8)$$

where $K_f$ is called the cryoscopic constant of the solvent.
Boiling Point Elevation:
By considering the liquid-vapor equilibrium in which the vapor contains only the component A, we can derive an expression analogous to that obtained above:

\[ \Delta T_b = \frac{RT_b^2M_A}{\Delta_{vap}H_m}m_B \quad \text{or} \quad \Delta T_b = K_b m_B \]  

(9)

where \( K_b \) is called the *ebullioscopic constant* of the solvent.

The elevation of boiling point is a rather weak effect compared to the depression of freezing point. Therefore, the latter property is overwhelmingly used for the practical applications of colligative properties.

Practical Applications:
- These equations are useful to determine the freezing points or boiling points of various solutions of nonvolatile solutes.
- A somewhat “liberal” interpretation of Eq. (6) or (7) can be used to calculate the solubility of various solutes at temperature \( T \) in a solvent whose enthalpy of fusion and freezing point are known.
- The “simplified” forms are also useful to determine the molar masses of unknown solutes using Eqs. (8) or (9).

Colligative properties depend on number of “particles” in solution rather than actual “concentration.” For instance, a 1 m solution of NaCl leads to a 2 m solution of ions (Na\(^+\) and Cl\(^-\)). Such a solution, therefore, will yield twice the expected \( \Delta T_f \). This effect must be taken into account when dealing with ionic substances.