

Phases, kinetics and non-equilibrium statistical mechanics

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Degrees of Freedom and Phases

PART

I

1 The Phase Rule

1.1 Phase

Definition 1.1. Phase, p , is a state of matter that is **uniform**¹ throughout in both chemical composition and physical states.

Phase numbers of common forms of matters

form of matter	number of phases
gas	$p=1$
solution	$p=1$
liquid	can be multiple phases
solid*	each solid of different chemical composition ² is in one phases

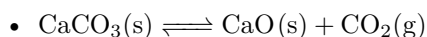
* One solid phase can contain different substances, e.g. steel, and in general, for alloys, $p = 1$ (but p may be greater than 1 in some cases).

1.2 Constituent and Components

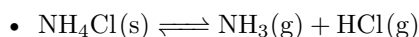
Definition 1.2. Constituent is a chemical species present.

Definition 1.3. Component, c , is *independent* constituent present.

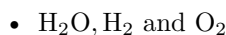
Example. To explain the meaning of *independent constituents*, some examples are provided below.



The number of constituents in the system is obviously 3. However, an reaction relates the three constituents, therefore, the number of components in the system is 2.



If no additional NH_3 or HCl is added to the system, $c = 3 - 1 - 1 = 1$. For except a restraint from the chemical reaction, there is another equation: $n(\text{NH}_3) = n(\text{HCl})$. And if additional NH_3 or HCl is added, $c = 2$.



c can be 1, 2 or 3. Although when the system is in equilibrium, $c = 3$ is impossible, under most conditions (e.g. 1 bar and room temperature), in the time scale we are considering, the equilibrium is hard to reach. And under these circumstances, $c = 3$ is possible to occur.

¹ When we talk about uniform, specified length and time scales are needed. If there are no specifications of these scales, the meaning of uniform itself becomes unclear. Usually, the specification is related to the problem we are discussing about.

² When the length scale of the system decreases into mesoscale, the chemical composition is hard to clarify and becomes very complex. So traditional phase theory can be hard to use in nano science.

1.3 Degrees of freedom

Definition 1.4. The **degree of freedom**, F , is the number of *intensive variables* that can be changed *independently* without disturbing the phase of the system.

Example. Some examples are given to show the identification of F .

- pure liquid water

For pure liquid water, the system itself can be explained by 4 variables, T, p, V, n , in which n is not an intensive variable and therefore can be ignored. The other three vars are restrained by the state equation, which gives out the result that for pure liquid water system, $F = 2$.

- mixture of liquid water and steam

The situation is similar to the example above, but there is another restrain function that $\mu(g) = \mu(s)$. So $F = 1$.

- mixture of water, steam and ice

Trivially $F = 0$.

- mixture of water and methanol

Other than T, p, V , x_1 is also intensive variable³. Two restrains exists, including the state equation and the equilibrium of chemical potential. Thus $F = 2$.

³ x_2 is not independent for $x_1 + x_2 = 1$

1.4 The phase rule

Theorem 1.1 (Phase rule). In thermodynamics, the **phase rule** is a general principle governing "pVT" systems (that is, systems whose states are completely described by the variables pressure (p), volume (V) and temperature (T)) in thermodynamic equilibrium. If F is the number of degrees of freedom, C is the number of components and P is the number of phases, then:

$$F = C - P + 2 \quad (1.1)$$

Proof. The Gibb's phase rule on the basis of the thermodynamic rule can be derived as follows:

First, let us consider a heterogeneous system consisting of P_n number of phases and C_n number of components in equilibrium. Let us assume that the passage of a component from one phase to another doesn't involve any chemical reaction. When the system is in equilibrium, it can be described by the following parameters:

- Temperature
- Pressure
- The composition of each phase

The total number of variables required to specify the state of the system is:

- Pressure: same for all phases
- Temperature: same for all phases
- Concentration

The independent concentration variables for one phase with respect to the C components is $C - 1$. Therefore, the independent concentration variables for P phases with respect to C components is $P(C - 1)$, thus the total number of variables is

$$P(C - 1) + 2$$

The various phases present in the system can only remain in equilibrium when the chemical potential (μ) of each of the component is the same in all phases. The number of equilibria for each P phases for each component is $P - 1$. For C components, the number of equilibria for P phases is $P(C - 1)$. Hence, the total number of equilibria involved is

$$C(P - 1)$$

Therefore,

$$F = [P(C - 1) + 2] - C(P - 1) = C - P + 2$$

□

2 The phase diagrams

2.1 Vapour pressure diagram

The partial vapour pressures of the components of an ideal solution of two volatile liquids are related to the composition of the liquid mixture by Raoult's law

$$p_A = x_A p_A^* \quad p_B = x_B p_B^*$$

where p_A^* and p_B^* are vapour pressures of pure A and B. The total vapour pressure p of the mixture is therefore

$$p = x_A p_A^* + x_B p_B^* = p_B^* + (p_A^* - p_B^*) x_A$$

2.1.1 The composition of the vapour

We define the fraction of A in the gas phase as y_A , similarly, y_B is the fraction of B in the vapour. Obviously,

$$y_i = \frac{p_i}{p} \quad i = A, B$$

It is trivial that

$$y_A = \frac{x_A p_A^*}{p_B^* + (p_A^* - p_B^*) x_A} \quad y_B = 1 - y_A$$

Simple derivation give out that

$$p = \frac{p_A^* p_B^*}{p_A^* + y_A (p_B^* - p_A^*)}$$

which can be plotted as below.

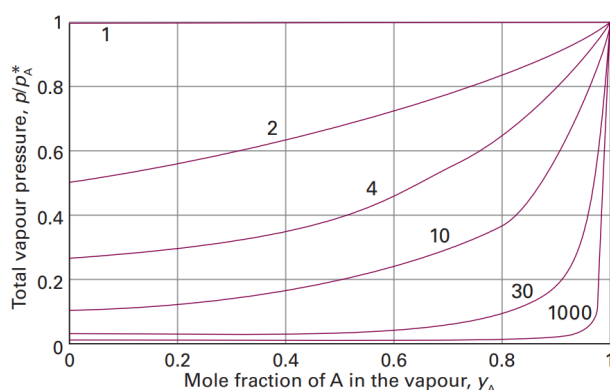


Figure 1. The dependence of the vapour pressure expressed in terms of the mole fraction of A in the vapour.

2.1.2 The interpretation of the diagrams

If we are interested in distillation, both the vapour and the liquid compositions are of equal interest. Thus we can plot the dependence of the total vapour pressure of an ideal solution on the mole fraction of A in the entire system.

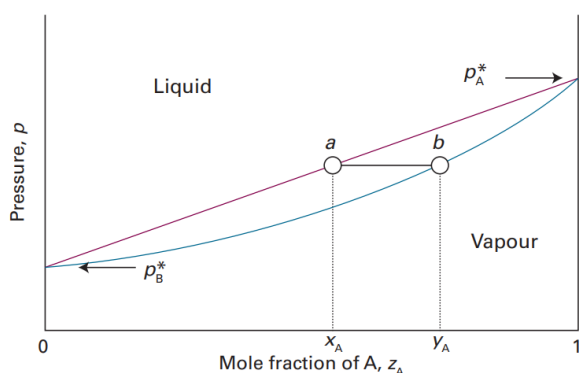


Figure 2. The dependence of the total vapour pressure of an ideal solution on the mole fraction of A in the entire system.

In the figure above, z_A is defined as

$$z_A = \frac{n_A(g) + n_A(l)}{n_A + n_B}$$

The point a indicates the vapour pressure of a mixture of composition x_A , and the point b indicates the composition of the vapour that is in equilibrium with the liquid at that pressure.

All the points down to the solid diagonal line in the graph correspond to a system that is under such high pressure that it contains only a liquid phase, so $z_A = x_A$, the composition of the liquid. On the other hand, all points below the lower curve correspond to a system that is under such low pressure that it contains only a vapour phase, so $z_A = y_A$.

Points that lie between the two lines correspond to a system in which there are two phases present, one a liquid and the other a vapour.

2.1.3 The lever rule

A point in the two-phase region of a phase diagram indicates not only qualitatively that both liquid and vapour are present, but represents quantitatively the relative amounts of

each. The relative amounts of two phases α and β can be found by using the lever rule⁴.

Theorem 2.1 (lever rule). The **lever rule** can be written as below:

$$n_{\alpha}l_{\alpha} = n_{\beta}l_{\beta}$$

where n_{α} is the amount of phase α and n_{β} is the amount of β , l_{α} and l_{β} represents the distance along the horizontal line, which is shown in the figure below.

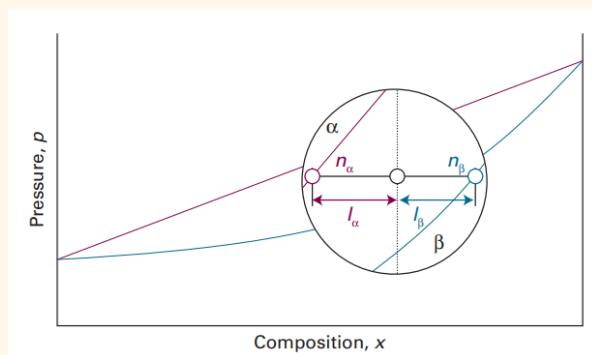


Figure 3. The lever rule

Proof. The proof of the lever rule is quite trivial. We mark the total amount of A and B as $n = n_{\alpha} + n_{\beta}$, where n_{α} is the amount of phase α and n_{β} is the amount of β . The mole fraction of A in phase α is $x_{A,\alpha}$, so the amount of A in α is $n_{\alpha}x_{A,\alpha}$. Similarly, The amount of A in β is $n_{\beta}x_{A,\beta}$, therefore

$$n_A = n_{\alpha}x_{A,\alpha} + n_{\beta}x_{A,\beta}$$

Also,

$$n_A = nz_A = n_{\alpha}z_A + n_{\beta}z_A$$

Just equating these two representations will give out the lever rule. \square

2.2 Temperature-composition diagrams

To discuss distillation we need a temperature-composition diagram, a phase diagram in which the boundaries show the composition of the phases that are in equilibrium at various temperatures. An example is given as Fig. 4.

2.2.1 Azeotropes

For real solutions, the temperature-composition diagram is always a little bit more complex than the diagram shown above. A maximum in the phase diagram (Fig. 5) may occur when the favourable interactions between A and B molecules reduce the vapour pressure of the mixture below the ideal value and so raise its boiling temperature: in effect, the A-B interactions stabilize the liquid. Some examples are CHCl_3 + propanone, nitric acid + H_2O .

⁴ The lever rule is so called because a similar rule relates the masses at two ends of a lever to their distances from a pivot.

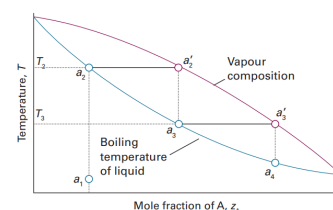


Figure 4. The temperature-composition diagram corresponding to an ideal mixture with the component A more volatile than component B.

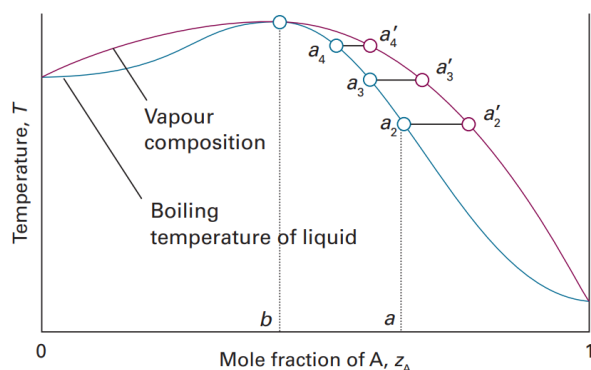


Figure 5. A high-boiling azeotrope.

Phase diagrams showing a minimum (Fig. 6) indicate that the mixture is destabilized relative to the ideal solution, the A–B interactions then being unfavourable. An example is $\text{H}_2\text{O} + \text{ethanol}$.

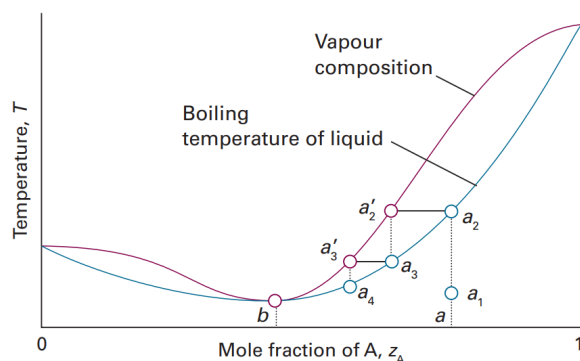


Figure 6. A low-boiling azeotrope.

Definition 2.1. An **azeotrope** or a constant boiling point mixture is a mixture of two or more liquids whose proportions cannot be altered or changed by simple distillation.

When an azeotrope is boiled, the vapour has the same proportions of constituents as the unboiled mixture. Each azeotrope has a characteristic boiling point. The boiling point of an azeotrope is either less than the boiling point temperatures of any of its constituents (a **positive azeotrope** or **low-boiling azeotrope**), or greater than the boiling point of any of its constituents (a **negative azeotrope** or **high-boiling azeotrope**).

2.3 Liquid-liquid phase diagram