2. *pressure at top and bottom*

An amount of argon (Ar, molar mass = 39.95 g·mole^{-1}) is contained in a vertical cylinder, with a piston at the upper side and 25 cm above the bottom of the vessel. The pressure exerted by the argon molecules on the piston is exactly 101325 Pa.

- Calculate the pressure exerted by the argon molecules on the bottom of the vessel; the temperature is 25 °C.

3. *Fahrenheit's temperature scale*

The temperature scale named after Daniel Gabriel Fahrenheit (1686-1736) was based on the two fixed points
i. the temperature of the cryogen mixture of water, ice and common salt (0 °F);
ii. the temperature of the human body (96 °F)
The Fahrenheit temperatures of the normal freezing point and the normal boiling point of water are 32 °F and 212 °F, respectively.

- Give the formula for the interconversion of Celsius and Fahrenheit temperatures and calculate the Celsius temperatures of Fahrenheit's fixed points.

4. *two phases and their amounts of two substances*

C and A are substances that are liquid at room temperature. When added together they give rise to two layers of liquid - a state of equilibrium between two liquid phases L_I and L_{II}.
In an experiment 10 mol A and 10 mol C are added together and it is established that L_I is composed of 6 mol A and 2 mol C and that, consequently, L_{II} is composed of 4 mol A and 8 mol C.

- Complete the table for three other experiments with other amounts of C and A, all expressed in mole.

added together		in phase L$_I$		in phase L$_{II}$	
$n(A)$	$n(C)$	$n(A)$	$n(C)$	$n(A)$	$n(C)$
10	10	6	2	4	8
5	5				
6	4				
2	8				

5. *ethanol and water saturate a space*

Assess the amounts of ethanol and water needed to saturate at 60 °C a space having a volume of 50 dm^3 such that the pressure exerted by the vapour - which is a mixture of ethanol and water - is 300 Torr.
It may be assumed that the vapour obeys the ideal-gas equation (←Table 3; Figure 2).

§ 003 THE RULES OF THE GAME

Obviously one cannot give an arbitrary value to each of the variables necessary to define the state of a system in equilibrium. It is examined how the number of independent variables can be found, once the equilibrium system has been defined.

independent and dependent variables

In the foregoing section we considered the equilibrium between liquid and vapour in a system of two substances. The state of the system in equilibrium, as we found, is fully defined by four variables, four intensive properties, which are temperature and pressure and for each of the two phases one composition variable. For the latter we took the mole fraction of the second component: X^{liq} for the liquid phase and X^{vap} for the vapour phase. At the end of the section we observed that, at constant temperature, the mole fractions of the liquid phase in equilibrium with vapour are represented by a curve in the *PX* plane. In other words, the mole fraction of a liquid phase in equilibrium with vapour can be represented as a function of pressure

$$X^{liq} = X^{liq}(P) \qquad T\ \text{const.}\ . \tag{1}$$

Similarly, there is a relation between pressure and the mole fraction of the vapour phase:

$$X^{vap} = X^{vap}(P) \qquad T\ \text{const.}\ . \tag{2}$$

Moreover, if one likes, one can replace the first of these expressions by

$$P = P(X^{liq}) \qquad T\ \text{const.}\ , \tag{3}$$

saying that the pressure indicated by the manometer is a function of the mole fraction of the liquid phase. And substitution of Equation (3) into Equation (2) gives rise to

$$X^{vap} = X^{vap}(X^{liq}) \qquad T\ \text{const.}\ . \tag{4}$$

The important observation we can make is, that for the equilibrium case considered, out of the three variables *P*, X^{liq} and X^{vap} only one can be freely chosen and that, thereafter, the remaining two are fixed. We are free to say that we want to realize that system such that X^{liq} = 0.2. Then we should know that in the case of Figure 002:2 the pressure can only have the value of 287.7 Torr and the mole fraction of the vapour phase the value of 0.547.

Generally, that is to say taking into account the influence of temperature as well, one can write

$$X^{liq} = X^{liq}\ (T, P) \qquad (5)$$

$$X^{vap} = X^{vap}\ (T, P) \qquad (6)$$

or, if one likes

$$P = P\ (T, X^{liq}) \qquad (7)$$

$$X^{vap} = X^{vap}\ (T, X^{liq}). \qquad (8)$$

Out of the four variables (T, P, X^{liq}, X^{vap}), two variables, say T and X^{liq} can be chosen - by the investigator - and after that choice, the remaining two are adjusted by the system itself.

In order to find out what really is going on with the variables involved in the liquid-vapour equilibrium, let's start again. Start again by taking a liquid mixture of the two substances, and, separated from it, a vapour mixture. The liquid mixture and the vapour mixture can be given different compositions and temperatures and put under different pressures: two times three variables that can be freely chosen. If we, next, bring the two together such that there will be equilibrium between a liquid and a vapour phase, we will observe that things are going to happen with the 2 x 3 = 6 values selected for the variables. First of all the *a priori equilibrium conditions* come into action, as a result of which the two phases will have a uniform temperature and a uniform pressure. At this 'moment' the number of variables involved has become four: four variables are needed to define the state of the system in equilibrium. These four variables constitute - what we are going to call - the *set M of variables*:

$$\mathrm{M} = \mathrm{M}\left[T, P, X^{liq}, X^{vap}\right]. \qquad (9)$$

Next, there is a set of (other) conditions that come into action: the *conditions of uniform chemical potentials* - the chemical potential of A in the liquid has to be equal to the chemical potential of A in the vapour, and the same holds true for B's potentials. The equilibrium conditions in terms of chemical potentials constitute the *set N of thermodynamic equilibrium conditions*:

$$\mathrm{N} = \mathrm{N}\left[\mu_A^{liq} = \mu_A^{vap}; \mu_B^{liq} = \mu_B^{vap}\right]. \qquad (10)$$

The influence of the two conditions is such - and that is purely mathematical - that four minus two variables remain as independent variables. In other terms and in harmony with the observations made above, in the equilibrium situation the values of X^{liq} and X^{vap} are fixed after the choice of T and P.

In the following we will use the symbols M and N, not only to refer to the two sets, but also for the numbers of elements in the two sets M and N, respectively. The number of independent variables of the system in equilibrium is found as

$$f = \mathrm{M}\left[T, P, X^{liq}, X^{vap}\right] - \mathrm{N}\left[\mu_A^{liq} = \mu_A^{vap}; \mu_B^{liq} = \mu_B^{vap}\right] = 4 - 2 = 2. \qquad (11)$$

The number f of independent variables is called the *number of degrees of freedom* or the *variance* of the equilibrium system. The equilibrium between liquid and vapour in a system of two substances is bivariant: has two degrees of freedom. If for these two degrees of freedom temperature and pressure are taken, then the type of mathematical solution of the set of N equations is

$$\left\{\begin{matrix} X^{liq} = X^{liq}\ (T, P) \\ X^{vap} = X^{vap}\ (T, P) \end{matrix}\right\}. \qquad (12)$$

It means that the solution of the set of N equations corresponds to two surfaces in *PTX* space which bear a certain relation to one another. One of the two surfaces represents the liquid phases and the other the vapour phases. Each pair of phases in equilibrium is represented by a point on the *liquidus surface* and a point on the *vaporus surface*, such that the line connecting the two points is parallel to the X axis. Figure 002:2 is an isothermal section of the two surfaces.

Generally, the chemical potentials figuring in the set N of thermodynamic equilibrium conditions are functions of the variables figuring in the M set. Therefore, in order to be able to solve the set of equations, one has to know - from case to case! - how the chemical potentials depend on the variables. One has to know, in other words what the *function recipes* are of the chemical potentials.

At this place it may be right to say a few words about the philosophy behind the construction of this work, in particular in relation to thermodynamics, the theoretical language of equilibria between phases. In level 1, the next part of the work, a start is made with thermo: to the extent that equilibria can be treated in which all phases are pure substances. In level 2 the thermodynamics of mixtures is introduced. In the first part of level 2, equilibria are considered for idealized cases such that the set of equilibrium equations can be solved in an analytical manner, read, such that explicit formulae can be derived for the M-*f* dependent variables in terms of the *f* independent variables. In the last three chapters of level 2, the systems considered are non-ideal, and, in order not to lose clarity, the complications related to the use of chemical potentials will be circumvented as much as possible. For the time being, that is to say in level 0, the approach will be of a phenomenological nature: without the use of thermodynamics; however, invariably starting from the thermo oriented sets M and N. The approach of this level is visualized in Scheme 1; again the binary liquid + vapour equilibrium and this time once more under isothermal conditions. An important role is reserved for expressions like the one represented by Equation (11) - for these expressions we will use the term *system formulation*.

The system

substances: A, B

equilibrium: A(liq) = A(vap); B(liq) = B(vap)

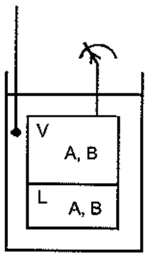
constraints: T is constant

the variables: $\mathrm{M} = \mathrm{M}\,[P, X^{liq}, X^{vap}]$

the conditions: $\mathrm{N} = \mathrm{N}\,[\mu^{liq} = \mu^{vap};\ \mu^{lq} = \mu^{vap}]$

the variance $f = \mathrm{M} - \mathrm{N} = 3 - 2 = 1$

type of solution $\begin{cases} X^{liq} = X^{liq}(T,P): & \text{curve in } PX \text{ plane} \\ X^{vap} = X^{vap}(T,P): & \text{curve in } PX \text{ plane} \end{cases}$



SCHEME 1. The isothermal binary liquid + vapour equilibrium

the phase rule

For the general equilibrium case of c components (substances) divided over the number p of phases, the number of degrees of freedom is, simply, given by

$$f = c - p + 2. \tag{13}$$

This relation, the so-called *Phase Rule*, is named after Josiah Willard Gibbs (1839-1903), the father of Phase Theory.

The phase rule can be derived, in a straightforward manner, by means of the M minus N approach - Scheme 2 may be of help.

	phases →	1	2	3	p
components ↓		α	β	γ	
1	A	x	x	x	$(p-1)$
2	B	x	x	x	$(p-1)$
3	C	x	x	x	$(p-1)$
c	number of mole fractions:	$(c-1)$	$(c-1)$	$(c-1)$	↑ number of conditions

SCHEME 2. On the derivation of the Phase Rule

In each phase there are $(c - 1)$ independent mole fractions, as a result, for p phases,

$$\mathrm{M} = \mathrm{M}\left[T, P \text{ and } p \text{ times } (c-1) \text{ mole fractions}\right]. \tag{14}$$

Next, the chemical potential of the substance A in phase α has to be equal to A's potential in each of the $(p - 1)$ other phases. The number of independent equilibrium conditions, the number of signs of equality is $(p - 1)$

$$\mu_A^{\alpha} = \mu_A^{\beta} = \mu_A^{\gamma} = \cdots\cdots\cdots = \mu_A^{\text{phase } p}. \tag{15}$$

As a result for all c substances

$$\mathrm{N} = \mathrm{N}[c \text{ times } (p-1) \text{ signs of equality}]. \tag{16}$$

The number of degrees of freedom now follows as

$$f = \mathrm{M} - \mathrm{N} = 2 + p\,(c-1) - c\,(p-1) = c + p - 2. \tag{17}$$

isothermal and/or isobaric conditions

Most generally, the liquid + vapour equilibrium in the system A + B has two degrees of freedom, as is shown by the (M - N) equation, Equation (11), and in agreement, of course, with the phase rule

$$f = c - p + 2 = 2 - 2 + 2 = 2. \tag{18}$$

In practice liquid+vapour equilibria are mostly studied either under *isothermal* or under *isobaric conditions*, which means that one of the two conditions has been consumed 'a priori'. If one likes one can say that for isobaric or isothermal conditions the phase rule reduces to

$$f = c - p + 1 \quad (T \text{ or } P \text{ constant}). \tag{19}$$

And similarly for both isothermal and isobaric conditions

$$f = c - p \quad (T \text{ and } P \text{ constant}). \tag{20}$$

It is not unlikely that the three different equations will give rise to some confusion. At any rate it is clear that the *system formulation*

$$f = \mathrm{M}\left[P, X^{liq}, X^{vap}\right] - \mathrm{N}\left[\mu_A^{liq} = \mu_A^{vap};\ \mu_B^{liq} = \mu_B^{vap}\right] = 1 \tag{21}$$

for the isothermal binary ($c = 2$) liquid + vapour equilibrium, does not give rise to any guesswork whatsoever.

the lever rule

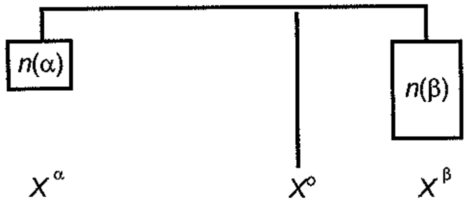
It may be emphasized that in the treatment as it is presented above it invariably is assumed that the equilibrium system has been realized and that, for that situation, the variables M and the conditions N are defined and the number of degrees of freedom are found. This is quite easy and quite straightforward. In practice, on the other hand, a series of obstacles has to be removed. The first of these is related to the amount of substance to be used.

It is clear that 1 drop of water is not enough to realize, say at 60 °C, the equilibrium between liquid and vapour in a space of 1 m^3.
It is also clear that it is impossible to realize the equilibrium between a vapour phase of (water + ethanol) having an ethanol mole fraction of 0.40 and a liquid phase of the two substances having an ethanol mole fraction of 0.08 by bringing equal amounts of the two substances in the experimental space. Indeed, that equilibrium can only be realized if the *overall mole fraction* of ethanol (X^o) is between 0.08 and 0.40, i.e. if $0.08 < X^o < 0.40$.

Generally, when $(1 - X^o)$ mol A and X^o mol B divide themselves over two phases α and β, having mole fractions values of X^α and X^β respectively, then the amounts of the two phases, $n(\alpha)$ and $n(\beta)$ respectively, satisfy the rule (→Exc 3):

$$n(\alpha):n(\beta)=(X^\beta - X^o):(X^o - X^\beta)\ . \qquad (22)$$

This rule is referred to as the *lever rule* or *centre of gravity principle.*



intellectual devices

In the treatment of phase equilibria, two popular intellectual devices are the *cylinder-with-piston* and the *vessel-with-manometer.* In the case of the first, the piston is weightless and able to move freely, without friction. The pressure exerted from the outside on the piston invariably is equal to the pressure inside. The experimentalist has the freedom to subject the system to the temperature and the pressure of his/her own choice. In the case of the second device, which is a vessel to which a manometer is connected (←Figure 002:1), the experimentalist has the freedom to adjust the temperature of the system. At the imposed temperature, the pressure is a property fixed by the equilibrium condition(s).

If an equilibrium system is defined by M variables and there are N equilibrium conditions, then the number of independent variables - the number of degrees of freedom - is f = M – N. For a system in which c substances give rise to an equilibrium between p phases that number is given by f = c – p + 2. This is the Phase Rule, named after Josiah Willard Gibbs.

EXERCISES

1. *three variables subjected to two conditions*

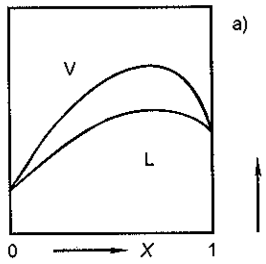
A certain system is characterized by the set of three variables M [X, Y, Z], which are subjected to the two conditions N [$f^{\mathrm{I}} = f^{\mathrm{II}}$; $g^{\mathrm{I}} = g^{\mathrm{II}}$], where f^{I} and f^{II} and g^{I} and g^{II} are functions of X, Y and Z:

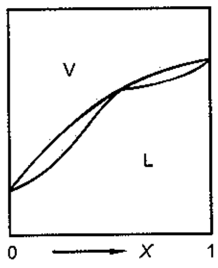
$f^{\mathrm{I}} = X + Y + Z$
$f^{\mathrm{II}} = 2X + 2Y + 2Z$
$g^{\mathrm{I}} = 3X + 2Y + 2Z$
$g^{\mathrm{II}} = X - Y - 2Z$

- Which relations do exist between the variables?

2. *phase diagram or not?*

Can Figure a) be a phase diagram of a binary system at isobaric conditions? And what is your opinion about Figure b) as a phase diagram?


a)


b)

3. *derivation of lever rule*

Show that when a mixture of two substances A and B, of which the overall mole fraction of B is equal to X^o, separates into a phase α of composition X^α and a phase β of composition X^β, the amount of substance in phase α and the amount of substance in phase β are related as

$$n(\alpha):n(\beta)=(X^\beta - X^o):(X^o - X^\alpha)$$

4. *a system formulation*

An empty space is filled, to about 50% of its volume, with equal amounts of three moderately volatile liquids A, B and C, which are pure substances that are partially miscible and give rise to three liquid phases.

- Determine the variance of this system at isothermal conditions, and so by first enumerating the M variables and the N equilibrium conditions.

5. *amounts of three phases out of three substances*

Starting with 1 mol A, 1 mol B and 1 mol C, the equilibrium is realized between the three phases α, β and γ. The mole fractions of B and C in each of the phases are given in the scheme below. For each of the phases, calculate its amount of substance.

phase	X_B	X_C
α	0.2	0.2
β	0.5	0.3
γ	0.1	0.6

6. *the experimental advantage of a small vapour phase*

A liquid mixture of water and ethanol, containing 20 mole percent of the latter, is brought a vessel-with-manometer. Next, the device is immersed in a thermostat adjusted at 60 °C. At this temperature the equilibrium is realized between liquid and vapour. It is estimated that the vapour phase occupies only 1 percent of the volume of the space.

- What is the pressure indicated by the manometer and what is the composition of the vapour?

Data are in § 002.

7. *naphthalene is added little by little to toluene*

In a continuous series of isothermal ($T = T_a$) vessel-with-manometer experiments 0.5 mole of naphthalene, which is solid at T_a, is added, little by little, to 0.5 mole of toluene. At the start of the series there is equilibrium between a liquid and a vapour phase, both composed of pure toluene. It is observed that, after the addition of 0.25 mol, naphthalene does not dissolve any more (the liquid has become saturated with naphthalene). In the final situation there is equilibrium between three phases: vapour (which is still pure toluene); liquid (saturated solution of naphthalene in toluene); and solid (pure naphthalene).

- Using straight lines, make a diagram in which the course of the pressure indicated by the manometer is plotted as a function of the overall mole fraction of naphthalene in the system (which increases from $X^o = 0$ to $X^o = 0.5$).

The following two (mutually related) general properties should be taken into account: 1) A's chemical potential, in a homogeneous mixture with B, decreases when B's mole fraction increases; and 2) the chemical potential of a gaseous substance increases with increasing pressure.

8. *does an empty place matter?*

In this section's derivation of the Phase Rule, it is assumed that each component is present in each of the phases - scheme 2.

- Is that necessary? Or, in other words, will the result $f = c - p + 2$ be influenced if one or more crosses are deleted from the scheme?