1

Physico-Chemical Transformations and Equilibria

A physico-chemical transformation of a system is the modification of the nature of its components under the influence of external stresses.

1.1. Characteristic parameters of physico-chemical transformations

A component is characterized by its chemical nature and by the phase to which it belongs. We can distinguish two types of physico-chemical transformations:

– physical transformations where there is no alteration of the chemical nature of the species but there is a modification of their phases;

– chemical transformations or reactions, where there is a modification of the chemical nature of the species present, and where that modification may or may not be accompanied by a phase change.

1.1.1. *Balance equation of a transformation*

Generally, a transformation is represented by its balance equation, which specifies the initial components, present before the transformation, and the end components. Symbolically, such a balance equation is written in the form:

$$0 = \sum_i \nu_i A_i \tag{1R.1}$$

This formulation shows the algebraic stoichiometric numbers v_i, which are counted as positive for the end components and as negative for the initial components. The sum is extended to all of the initial and final components.

Physical transformations are characterized by the unit value of all the stoichiometric numbers.

It is often useful for the balance equation to show the nature of the phases in which the components are. In order to do this, a system of symbols as outlined in Table 1.1 is included in the balance equations. According to this system, the vaporization of pure liquid water in an atmosphere composed solely of water is written as:

$$\left(H_2O\right) = \{H_2O\} \tag{1R.2}$$

Symbol	Meaning	Symbol	Meaning
{A}	Pure A in a gaseous phase	{{A}}	A in a gaseous mixture
(A)	Pure A in a liquid phase	((A))	A in a liquid solution
<A>	Pure A in a solid phase	<<A>>	A in a solid solution

Table 1.1. *Symbolic representation of the phases of components in balance equations*

The vaporization of water in air on the basis of a liquid solution is written as:

$$\left(\left(H_2O\right)\right) = \{\{H_2O\}\} \tag{1R.3}$$

1.1.2. *Values associated with a transformation*

To each transformation, for any extensive value A, we attribute a value, written as $\Delta_r A$, called A associated with the transformation r. This value is defined, on the basis of the partial molar values $\overline{A_i}$ of the components involved in the transformation, by the relation:

$$\Delta_r A = \sum_i v_i \overline{A_i} \tag{1.1}$$

Thus, we speak of the enthalpy, Gibbs energy, entropy, variations in volume, etc. associated with the transformation.

1.1.3. *Standard values associated with a transformation*

We shall see that in the particular case where we choose pure components in their phases, at a pressure of 1 bar, the *standard value A associated with the reaction* [1R.1] is defined by the relation:

$$\Delta_r A^0 = \sum_i v_i a_i^o \qquad [1.2]$$

a_i^o is the *standard value of the parameter A of the i*, meaning that the value of A taken in the pure state at a pressure of 1 bar at the temperature of 298 K (25ºC), the substance being in its normal state of condensation at that temperature and pressure. We thus define a *standard value at temperature T* as the above standard value chosen at the temperature T instead of 298 K.

1.1.4. *Extent and rate of a transformation*

A transformation is also characterized by its extent ξ at a time t and its rate $\Re$ at that instant. The rate is the derivative in relation to time of the extent. If n_k is the number of moles of the component A_k, we have:

$$\frac{d\xi}{dt} = \frac{1}{v_k}\frac{dn_k}{dt} \qquad [1.3a]$$

and:

$$\Re = \frac{d\xi}{dt} \qquad [1.3b]$$

In the case where multiple transformations take place in the system, equations [1.3a] and [1.3b] are replaced by:

$$\frac{dn_{k_\rho}}{dt} = v_{k_\rho} \Re_\rho \qquad [1.4a]$$

and:

$$\frac{\mathrm{d}\,n_k}{\mathrm{d}\,t} = \sum_{\rho} v_{k_\rho} \mathfrak{R}_\rho \qquad \text{[1.4b]}$$

In these expressions, $\mathrm{d}\,n_{k_\rho}$, $\mathfrak{R}_\rho$ and v_{k_ρ} respectively denote the variation of the quantity of the component A_k due to the transformation ρ, the rate of the transformation ρ and the stoichiometric number relative to component A_k in the transformation ρ. The sum of relation [1.4b] is found for all of the transformations taking place in the system under study.

1.2. Entropy production during the course of a transformation in a closed system

Consider the transformation [1R.1]. We respectively denote by $\mathrm{d}_i\,S$ and $\mathrm{d}_e\,S$ the contributions to the entropy variation made by the entropy production within the system and the exchanges with the external medium. The entropy balance at each moment can be written as:

$$\frac{\mathrm{d}\,S}{\mathrm{d}\,t} = \frac{\mathrm{d}_i\,S}{\mathrm{d}\,t} + \frac{\mathrm{d}_e\,S}{\mathrm{d}\,t} \qquad \text{[1.5]}$$

For our study, we choose as variables the p pertinent intensive variables Y_k and the quantities of material whose fluxes are reduced, in a closed system, according to relation [1.3], to the derivative of the extent of the reaction. We can therefore express the entropy flux on the basis of those variables, so:

$$\frac{\mathrm{d}\,S}{\mathrm{d}\,t} = \sum_{k=1}^{p} \frac{\partial S}{\partial Y_k} \frac{\mathrm{d}\,Y_k}{\mathrm{d}\,t} + \frac{\partial S}{\partial \xi} \frac{\mathrm{d}\,\xi}{\mathrm{d}\,t} \qquad \text{[1.6]}$$

In addition, the entropy contribution due to the exchanges with the external environment is linked to the exchanged heat, by:

$$\frac{\mathrm{d}_e\,S}{\mathrm{d}\,t} = \frac{1}{T} \frac{\mathrm{d}\,Q}{\mathrm{d}\,t} \qquad \text{[1.7]}$$

This exchanged heat is expressed as a function of the variables by way of the specific heat coefficients χ_k, which enables us to write the following for the entropy flux exchanged:

$$\frac{\mathrm{d}_e S}{\mathrm{d}t} = \sum_{k=1}^{p} \frac{\chi_k}{T} \frac{\mathrm{d}Y_k}{\mathrm{d}t} + \frac{\chi_T}{T} \frac{\mathrm{d}\xi}{\mathrm{d}t} \qquad [1.8]$$

By comparing expressions [1.6] and [1.8], we obtain the contribution of the internal production to the variation in entropy as a function of the system variables:

$$\frac{\mathrm{d}_i S}{\mathrm{d}t} = \sum_{k=1}^{p} \left(\frac{\partial S}{\partial Y_k} - \frac{\chi_k}{T} \right) \frac{\mathrm{d}Y_k}{\mathrm{d}t} + \left(\frac{\partial S}{\partial \xi} - \frac{\chi_T}{T} \right) \frac{\mathrm{d}\xi}{\mathrm{d}t} \qquad [1.9]$$

According to the second law, this entropy production must be positive or null in any spontaneous transformation. If we envisage a transformation whereby the external intensive variables Y_k are kept constant, if the transformation is spontaneous, it means that we satisfy the inequality:

$$\frac{\mathrm{d}_i S}{\mathrm{d}t} = \left(\frac{\partial S}{\partial \xi} - \frac{\chi_T}{T} \right) \frac{\mathrm{d}\xi}{\mathrm{d}t} \geq 0 \qquad [1.10]$$

Thus, expression [1.10] is a condition needing to be fulfilled during any real transformation keeping the intensive variables Y_k constant.

1.3. Affinity of a transformation

We shall introduce a new value – the affinity – pertaining to any transformation. The variables for this affinity are the (intensive or extensive) Thermodynamic variables, the quantities of material and the extent of the transformation.

1.3.1. *Definition*

De Donder proposed to use the term *affinity* of the transformation, denoted as $\mathscr{A}$, for the entity:

$$\mathscr{A} = T \left(\frac{\partial S}{\partial \xi} - \frac{\chi_T}{T} \right) \qquad [1.11]$$

According to expression [1.10], the entropy production can be expressed on the basis of that activity by:

$$\frac{d_i S}{dt} = \frac{\mathscr{A}}{T} \frac{d\xi}{dt}$$ [1.12]

On the basis of this definition, we shall be able to express the affinity another way.

1.3.2. *Affinity and characteristic functions*

The variation of internal energy is, according to the first law of thermodynamics:

$$\frac{dU}{dt} = \frac{dQ}{dt} + \frac{dW}{dt} = T\frac{d_e S}{dt} + \frac{dW}{dt} = T\frac{dS}{dt} - T\frac{d_i S}{dt} + \frac{dW}{dt}$$ [1.13]

If all the exchanges are reversible, apart from the transformation under study (we then say that the system is at physical equilibrium), then the work term is written:

$$\frac{dW}{dt} = \sum_{k=2}^{p} Y_k dX_k$$ [1.14]

The sum that appears in the above expression is extended to all couples of conjugate variables, with the exception of the temperature–entropy couple (which is why the index k begins at the value of 2). By substituting this back into expression [1.13] and taking account of relation [1.12], we obtain:

$$\frac{dU}{dt} = \sum_{k=2}^{p} Y_k \frac{dX_k}{dt} + T\frac{dS}{dt} - \mathscr{A}\frac{d\xi}{dt}$$ [1.15]

This gives us a new expression of the affinity, which is therefore the opposite of the differential of the function U in relation to the fractional extent with constant entropy and extensive variables:

$$\mathscr{A} = -\left(\frac{\partial U}{\partial \xi}\right)_{S, X_k}$$ [1.16]

We can generalize this expression for any characteristic function Γ, defined by:

$$\Gamma = U - TS - \sum_{i=2}^{q} X_i Y_i \quad \text{where } 2 \leq q \leq p \qquad [1.17]$$

By differentiation of [1.17], we obtain:

$$d\Gamma = dU - T\,dS - S\,dT - \sum_{i=2}^{q} X_i\,dY_i - \sum_{i=2}^{q} Y_i\,dX_i \qquad [1.18]$$

Thus, when we consider relation [1.15]:

$$d\Gamma = -S\,dT - \sum_{i=2}^{q} X_i\,dY_i + \sum_{m=q+1}^{p} Y_m\,dX_m - \mathscr{A}\,d\xi \qquad [1.19]$$

we obtain a new expression of the affinity which generalizes relation [1.16]:

$$\mathscr{A} = -\left(\frac{\partial \Gamma}{\partial \xi}\right)_{X_m Y_l T} \qquad [1.20]$$

In particular, for chemical systems with the variables pressure and temperature, the characteristic function is the Gibbs energy G. We obtain:

$$\mathscr{A} = -\left(\frac{\partial G}{\partial \xi}\right)_{P,T} \qquad [1.21]$$

At constant pressure and temperature, the affinity is the opposite of the partial derivative of the Gibbs energy in relation to the extent.

NOTE 1.1.– Expression [1.15] shows that the affinity, which is an extensive value, and the extent, which is an intensive value, are two conjugate values.

1.3.3. *Affinity and chemical potentials*

If we consider relation [1.3], we can write:

$$\left(\frac{\partial G}{\partial \xi}\right)_{P,T} = \sum_{i} v_i \left(\frac{\partial G}{\partial n_i}\right)_{P,T,n_j} = \sum_{i} v_i \mu_i \qquad [1.22]$$

By substituting this back into relation [1.21], we obtain an expression of the affinity as a function of the chemical potentials of the components involved in the transformation:

$$\mathscr{A} = -\sum_i \nu_i \mu_i \qquad\qquad [1.23]$$

The affinity of a transformation therefore depends only on the chemical potentials of the components involved in that transformation.

Using expression [1.22], we can write:

$$\sum_i \nu_i \left(\frac{\partial G}{\partial n_i} \right)_{P,T,n_j} = \sum_i \nu_i \overline{G}_i = \Delta_r G = \sum_i \nu_i \mu_i \qquad\qquad [1.24]$$

Thus, by comparing this with relation [1.23]:

$$\Delta_r G = -\mathscr{A} \qquad\qquad [1.25]$$

The affinity of a transformation is thus the opposite of the Gibbs energy associated with that transformation.

These results can easily be generalized to any general Gibbs energy using the generalized chemical potentials which correspond to it. For example, for the electrochemical Gibbs energy and the electrochemical potentials, an expression such as [1.23] will give the electrochemical affinity of an electrochemical reaction.

1.3.4. *Affinity, reaction quotient and activities*

If, in relation [1.23], we explicitly state the chemical potentials of the species in solution in the form:

$$\mu_i = \mu_i^0 + RT \ln a_i \qquad\qquad [1.26]$$

for the transformation [1R.1], we find the expression of the affinity as a function of the activities:

$$\mathscr{A} = -\sum_i \nu_i \mu_i^0 - RT \prod_i a_i^{\nu_i} \qquad\qquad [1.27]$$

If we define the value Q_r, known as the *reaction quotient* of the transformation r, by the relation:

$$Q_r = \prod_i a_i^{v_i} \qquad [1.28]$$

then the affinity takes the form:

$$\mathscr{A} = \mathscr{A}^0 - RT \ln Q_r \qquad [1.29]$$

Using relation [1.25], the Gibbs energy associated with the reaction takes the form:

$$\Delta_r G = \Delta_r G^0 + RT \ln Q_r \qquad [1.30]$$

The last two relations will be useful for the expression of the equilibrium constants (see section 3.1).

1.3.5. *Total differential of the affinity in variables Y_l, X_m, ξ*

As the affinity is a function of state, its differential, expressed on the basis of the chosen variables, will be of the form:

$$\mathrm{d} A = \sum_l \frac{\partial \mathscr{A}}{\partial Y_l} \mathrm{d} Y_l + \sum_m \frac{\partial \mathscr{A}}{\partial X_m} \mathrm{d} X_m + \frac{\partial \mathscr{A}}{\partial \xi} \mathrm{d} \xi \qquad [1.31]$$

Using relation [1.20], we find:

$$\frac{\partial \mathscr{A}}{\partial \xi} = -\frac{\partial^2 \Gamma}{\partial \xi^2} \qquad [1.32]$$

and by applying equation [1.23]:

$$\frac{\partial \mathscr{A}}{\partial Z} = -\sum_i v_i \frac{\partial \mu_i}{\partial Z} \qquad [1.33]$$

with Z being one of the variables in the set (Y_l, X_m).

In the case where that set of variables comprises only intensive variables Y_l, the differential of the affinity is written:

$$dA = \sum_l \frac{\partial \mathscr{A}}{\partial Y_l} dY_l + \frac{\partial \mathscr{A}}{\partial \xi} d\xi \qquad [1.34]$$

However, by applying relation [1.33] and the symmetry of the characteristic matrix, if X_l is the conjugate extensive value of Y_l, we obtain:

$$\frac{\partial A}{\partial Y_l} = \sum_i v_i \overline{X}_{l_{i_i}} = \Delta_r X_l \qquad [1.35]$$

This gives us the differential of the affinity in intensive variables (partial molar values) and extent:

$$d\mathscr{A} = \Delta_r X_l \, dY_l + \frac{\partial \mathscr{A}}{\partial \xi} d\xi \qquad [1.36]$$

Let us apply these results to chemical systems with variables $-P$, T, so then equation [1.35] gives us:

$$\frac{\partial \mathscr{A}}{\partial T} = \sum_i v_i \overline{S}_{i_i} = \Delta_r S \qquad [1.37]$$

In addition, we have:

$$\frac{\partial \mathscr{A}}{\partial P} = -\sum_i v_i \overline{V}_{i_i} = -\Delta_r V \qquad [1.38]$$

The differential of the affinity then becomes:

$$d\mathscr{A} = \Delta_r S \, dT - \Delta_r V \, dP - \frac{\partial^2 G}{\partial \xi^2} d\xi \qquad [1.39]$$

NOTE 1.2.– Helmholtz's second relation gives the derivative of the ratio μ_i/T with the temperature:

$$\left[\frac{\partial \left(\dfrac{\mu_i}{T} \right)}{\partial T} \right]_{P,\xi} = \frac{\overline{H}_{i_i}}{T^2} \qquad [1.40]$$

By coupling this relation with expression [1.23], we obtain:

$$\left[\frac{\partial\left(\dfrac{\mathscr{A}}{T}\right)}{\partial T}\right]_{P,\xi} = \frac{\sum_i v_i \, \overline{H}_{i_i}}{T^2} = \frac{\Delta_r H}{T^2} \qquad [1.41]$$

$\Delta_r H$ is the enthalpy associated with the transformation studied.

1.3.6. *Derivatives of the affinity in relation to the extent and the chemical potentials*

By deriving equation [1.23], we obtain:

$$\frac{\partial\mathscr{A}}{\partial\xi} = -\sum_i v_i \frac{\partial\mu_i}{\partial\xi} \qquad [1.42]$$

However, by taking account of relation [1.3], we can write:

$$\frac{\partial\mu_i}{\partial\xi} = \sum_{k=1}^{N} \frac{\partial\mu_k}{\partial n_k}\frac{\partial n_k}{\partial\xi} = \sum_k v_k \frac{\partial\mu_i}{\partial n_k} \qquad [1.43]$$

Thus:

$$\frac{\partial\mathscr{A}}{\partial\xi} = -\sum_k\sum_i v_k v_i \frac{\partial\mu_i}{\partial n_k} \qquad [1.44]$$

which can be expressed in the form:

$$\frac{\partial\mathscr{A}}{\partial\xi} = -\sum_k\sum_{k\neq i} v_k v_i \frac{\partial\mu_i}{\partial n_k} + \sum_i v_i^2 \frac{n_i^2}{n_i^2}\frac{\partial\mu_i}{\partial n_i} \qquad [1.45]$$

However, according to the Gibbs-Duhem relation, we have:

$$n_i \frac{\partial\mu_i}{\partial n_i} = -\sum_{k\neq i} n_k \frac{\partial\mu_k}{\partial n_i} \qquad [1.46a]$$

The symmetry of the characteristic matrix leads to:

$$\frac{\partial \mu_i}{\partial n_k} = \frac{\partial \mu_k}{\partial n_i} \qquad [1.46b]$$

Thus, by substituting the expressions [1.46a] and [1.46b] into expression [1.45], we find:

$$\frac{\partial \mathscr{A}}{\partial \xi} = -\sum_k \sum_{k \neq i} v_k v_i \frac{\partial \mu_i}{\partial n_k} + \sum_i \sum_{k \neq i} v_i^2 \frac{n_i n_k}{n_i^2} \frac{\partial \mu_i}{\partial n_i} \qquad [1.47]$$

By decomposing the second term, this expression takes the form:

$$\frac{\partial \mathscr{A}}{\partial \xi} = -\sum_k \sum_{k \neq i} v_k v_i \frac{\partial \mu_i}{\partial n_k} - \frac{1}{2}\sum_i \sum_{k \neq i} v_i^2 \frac{n_i^2}{n_i^2} \frac{\partial \mu_i}{\partial n_i} + \frac{1}{2}\sum_i \sum_{k \neq i} v_k^2 \frac{n_i^2}{n_i^2} \frac{\partial \mu_i}{\partial n_k}$$

We can verify that the above formula is equivalent to:

$$\frac{\partial \mathscr{A}}{\partial \xi} = \frac{1}{2}\sum_i \sum_k \frac{\partial \mu_i}{\partial n_k}\left(\frac{v_i}{n_i} - \frac{v_k}{n_k}\right)^2 n_i n_k \qquad [1.48]$$

This expression gives us the derivative of the affinity in relation to the extent as a function of the derivatives of the chemical potentials of the components of the reaction in relation to the quantities of the other materials.

1.4. De Donder's inequality – direction of the transformations and equilibrium conditions

The second principle, applied to relation [1R.1], gives us:

$$\frac{\mathscr{A}}{T}\frac{d\xi}{dt} \geq 0 \qquad [1.49]$$

In this inequality, we see the appearance of the rate of reaction (expression [1.2]), which is tantamount to writing that in order for a transformation to be possible, it is necessary for the affinity and rate to obey the condition:

$$\mathscr{A}\mathfrak{R} \geq 0 \qquad [1.50]$$

This inequality constitutes *de Donder's inequality*, which is a general formulation of the condition of transformation and does not depend on the set of variables chosen.

We shall now discuss this inequality:

– if the affinity is positive, we need to have a positive or null rate to respect the condition [1.50]. If the rate is positive, this means that the transformation takes place from left to right in the chosen formula. If the rate is zero, the transformation does not happen;

– if the affinity is negative, the inequality gives a negative or null rate, and the transformation will take place spontaneously from right to left of the chosen formula, or will not take place;

– if the affinity is null, then the rate is null because, if such were not the case, the system would be the seat of a reversible transformation (null entropy production) with a non-null rate, which is incompatible with the definition of a reversible transformation.

Let us now examine the reciprocal of our discussion:

– if the rate is positive then inequality [1.50] necessarily leads to a positive affinity. The affinity cannot be null because we would still have a reversible transformation at non-null rate;

– if the rate is negative, then the affinity is also negative, with the reverse reaction occurring;

– if the rate is null, then the system is at equilibrium. We can therefore have either a null or a non-null affinity. In the first case (null affinity), we say that the system is at *thermodynamic equilibrium*. In the second case (non-null affinity), the system is said to be at *false equilibrium*. False equilibrium is thus encountered for a transformation which does not take place although its affinity is positive. For instance, we can cite the synthesis of water under normal conditions of temperature and pressure. The hydrogen-oxygen mixture does not react. Its rate is too slow for the reaction to be perceptible. In such a case, we could use a catalyst to carry out such a transformation, which would not alter the affinity but would modify the rate. The choice of a catalyzer is useless and ineffectual if the affinity is null or negative.

Thus, the necessary and sufficient condition of thermodynamic equilibrium is, by definition:

$$\mathscr{A} = 0 \qquad\qquad [1.51]$$

and the true meaning of the possibility of occurrence of the transformation is given by the condition:

$$\mathscr{A} > 0 \qquad\qquad [1.52]$$

In light of relations [1.23] and [1.24], these conditions are also written:

For thermodynamic equilibrium:

$$\Delta_r G = 0 \qquad\qquad [1.53]$$

or:

$$\sum_{k=1}^{N} \nu_k \mu_k = 0 \qquad\qquad [1.54]$$

For the direction of spontaneous reaction:

$$\Delta_r G < 0 \qquad\qquad [1.55]$$

or:

$$\sum_{k=1}^{N} \nu_k \mu_k < 0 \qquad\qquad [1.56]$$

These conditions are independent of the nature of the physico-chemical transformation and the variables chosen to define the system, provided that system is home only to a single transformation.

1.5. Heats of transformation

Usually, transformations involve heat exchanges with the outside environment, which may be due to heat being released (exothermic transformations) or absorbed (in the case of endothermic transformations). We shall express those heat exchanges in two important cases.

1.5.1. *Heat of transformation at constant pressure and temperature*

We can express the elementary heat of a transformation in the form:

$$\delta Q = T \, \mathrm{d}_e S = T \, \mathrm{d} S - T \, \mathrm{d}_i S \qquad [1.57]$$

By choosing all the variables $(T, -P, \xi)$, we shall have:

$$\delta Q = T \frac{\partial S}{\partial T} \mathrm{d} T + T \frac{\partial S}{\partial P} \mathrm{d} P + T \frac{\partial S}{\partial \xi} \mathrm{d}\xi - T \, \mathrm{d}_i S \qquad [1.58]$$

At constant pressure and temperature, this gives us:

$$\delta Q_P = T \frac{\partial S}{\partial \xi} \mathrm{d}\xi - T \, \mathrm{d}_i S \qquad [1.59]$$

However, as the generalized Gibbs energy Γ is a function of state, we have, according to relation [1.19]:

$$\left(\frac{\partial S}{\partial \xi} \right)_{P,T} = - \left(\frac{\partial \mathscr{A}}{\partial T} \right)_{P,\xi} \qquad [1.60]$$

Thus, we can write relation [1.59] in the form:

$$\delta Q_P = - \left[T \left(\frac{\partial \mathscr{A}}{\partial T} \right)_{P,\xi} + \mathscr{A} \right] \mathrm{d}\xi \qquad [1.61]$$

By integrating this expression for the whole of the transformation, we obtain:

$$Q_P = \int_{\xi=0}^{\xi=\infty} \delta Q_P = - \left[T \left(\frac{\partial \mathscr{A}}{\partial T} \right)_{P,\xi} + \mathscr{A} \right] \qquad [1.62]$$

By replacing the affinity with its expression [1.22], we find:

$$Q_P = T \sum_k v_k \frac{\partial \mu_k}{\partial T} + \sum_k v_k \mu_k \qquad [1.63]$$

Thus, by using the symmetry of the characteristic matrix:

$$Q_P = T \sum_k v_k \overline{S}_k + \sum_k v_k \mu_k \qquad [1.64]$$

However, we know that we have:

$$\mu_k = \overline{G}_k = \overline{H}_k - T\overline{S}_k \qquad [1.65]$$

For the heat of reaction we find:

$$Q_P = \sum_k v_k \overline{H}_k = \Delta_r H \qquad [1.66]$$

Thus, the heat of transformation, at constant temperature and pressure, is equal to the enthalpy associated with the reaction.

NOTE 1.3.– For a long time, chemists counted the heat released by an exothermic reaction positively. With this old convention, relation [1.66] was transformed into:

$$Q_P = -\Delta_r H$$

1.5.2. Heat of transformation at constant volume and temperature

Let us look again at expression [1.58]. By choosing the set of variables (T, V, ξ), we obtain:

$$\delta Q = T \frac{\partial S}{\partial T} \mathrm{d}T + T \frac{\partial S}{\partial V} \mathrm{d}V + T \frac{\partial S}{\partial \xi} \mathrm{d}\xi - T \mathrm{d}_i S \qquad [1.67]$$

At constant volume and temperature we have:

$$\delta Q_V = T \frac{\partial S}{\partial \xi} \mathrm{d}\xi - T \mathrm{d}_i S \qquad [1.68]$$

By applying the same reasoning as in the previous section (see section 1.5.1), we find:

$$Q_V = T \sum_k v_k \left(\frac{\partial S}{\partial n_k} \right)_{V,T,n_j} + \sum_k v_k \mu_k \qquad [1.69]$$

However, we know that:

$$\mu_i = \left(\frac{\partial F}{\partial n_k} \right)_{V,T,n_j} \qquad [1.70]$$

Thus:

$$Q_V = T \sum_k v_k \left(\frac{\partial S}{\partial n_k} \right)_{V,T,n_j} + \sum_k v_k \left(\frac{\partial F}{\partial n_k} \right)_{V,T,n_j} \qquad [1.71]$$

and, taking account of:

$$F = U - TS \qquad [1.72]$$

the heat of transformation is:

$$Q_V = \sum_k v_k \left(\frac{\partial U}{\partial n_k} \right)_{V,T,n_j} = \Delta_r U \qquad [1.73]$$

Thus, the heat of transformation, at constant temperature and volume, is equal to the internal energy associated with the reaction.

1.5.3. *Variations in the heat of transformation at constant pressure with changing temperature – Kirchhoff relation*

According to equation [1.66], we can write:

$$\left(\frac{\partial Q_P}{\partial T} \right)_P = \sum_k v_k \left(\frac{\partial \overline{H}_k}{\partial T} \right)_{P_j} \qquad [1.74]$$

However, the differential of the partial molar enthalpy can be expressed in the form:

$$d\overline{H}_k = T\,dS_k + \overline{V}_k\,dP + \sum_k \mu_k\,dn_k \qquad [1.75]$$

Thus, at a given pressure and extent, we obtain:

$$\left(\frac{\partial \overline{H}_k}{\partial T}\right)_{P_j} = T\left(\frac{\partial \overline{S}_k}{\partial T}\right)_{P_j} = \overline{C}_{P_k} \qquad [1.76]$$

By substituting that equation back into relation [1.74], we find:

$$\left(\frac{\partial Q_P}{\partial T}\right)_P = \sum_k v_k \overline{C}_{P_k} = \Delta_r C_P \qquad [1.77]$$

This relation constitutes what we call the *Kirchhoff relation*. An equivalent relation would give the variation of the heat of transformation at constant volume with the temperature as a function of the molar specific heat capacity at constant volume associated with the transformation.

1.6. Set of points representing the equilibrium states of a transformation

Consider a transformation at thermodynamic equilibrium for given values of the variables of state. Its affinity is null. If we vary one or more of the variables of state by an infinitesimal amount, the affinity takes on a new value $\mathscr{A} + d\mathscr{A}$. In order for that new state to also be a state of equilibrium of transformation, it is necessary for that new value of the affinity to be null, so:

$$\mathscr{A} + d\mathscr{A} = 0 \qquad [1.78]$$

This leads us to:

$$d\mathscr{A} = 0 \qquad [1.79]$$

By stating the affinity on the basis of the chemical potentials of the N components involved in the transformation, the condition becomes:

$$\sum_{k=1}^{N} \nu_k \, d\mu_k = 0 \qquad [1.80]$$

Either of these last two expressions, [1.79] and [1.80], enables us to define the set of equilibrium states of the transformation.

1.7. Closed systems accommodating multiple reactions

Consider a system in which, between the components, there are R possible transformations. A component may not necessarily be involved in multiple kinds of transformations (in a transformation in which it is not involved, its stoichiometric coefficient will be zero). For the ρth transformation, we can define an affinity according to relation [1.11], and by applying relation [1.23], we find:

$$\mathscr{A}_\rho = -\sum_k \nu_{k_\rho} \mu_k \qquad [1.81]$$

If ν_{k_ρ} is the stoichiometric number of component A_k in the ρth transformation, then by pursuing the same reasoning as in section 1.3.2, with ξ_ρ representing the extent of the reaction ρ, we obtain:

$$\mathscr{A}_\rho = -\frac{\partial \Gamma}{\partial \xi_\rho} \qquad [1.82]$$

The real transformation condition, therefore, will be:

$$d\Gamma = -\sum_\rho \mathscr{A}_\rho \, d\xi_\rho \leq 0 \qquad [1.83]$$

and consequently:

$$\sum_\rho \mathscr{A}_\rho \frac{d\xi_\rho}{dt} = \sum_\rho \mathscr{A}_\rho \mathfrak{R}_\rho \geq 0 \qquad [1.84]$$

This inequality is a generalization of De Donder's inequality (see section 1.4). We can see that, for a transformation to be possible, it is no longer necessary for inequality [1.50] to be satisfied, if that transformation occurs in a system which contains multiple transformations, and such that relation [1.84] will, itself, be satisfied. This phenomenon of a reaction which is impossible on its own but is possible within a set of transformations, in the same conditions, is known as *chemical coupling*.

At thermodynamic equilibrium, the sum appearing in relation [1.83] must be zero, implying that all the individual terms $\mathscr{A}_\rho$ are zero regardless of the transformation at hand. The condition of equilibrium of transformations in the system, for any transformation ρ belonging to the set R, will therefore be:

$$\mathscr{A}_\rho = 0 \qquad [1.85]$$

NOTE 1.4.– We shall see (in section 2.2) that this condition is sufficient but not necessary if not all the transformations are independent.

1.8. Direction of evolution and equilibrium conditions in an open system

In an open system, the variations dn_k in the amount of component A_k are no longer linked to one another by the transformation; these quantities can also change because of exchanges of matter with the external environment. In a chemical system, the variation of Gibbs energy is written in the form:

$$dG = -S\,dT + V\,dP + \sum_{k=1}^{N} \mu_k \, dn_k \qquad [1.86]$$

For equilibria at temperature and pressure that are both kept constant, the Gibbs energy is a potential function and therefore in order for the system to be able to evolve spontaneously, we need:

$$dG = \sum_{k=1}^{N} \mu_k \, dn_k \leq 0 \qquad [1.87]$$

At thermodynamic equilibrium, the potential function reaches an extremum. If that extremum is a minimum, then the equilibrium is stable. If

the extremum is a maximum, then the equilibrium is unstable (see section 2.6.2).

At equilibrium, we therefore ought to have:

$$\sum_{k=1}^{N} \mu_k \, dn_k = 0 \tag{1.88}$$

This relation is a generalization of relation [1.54], which takes that form when we remember that, in a closed environment where only a single transformation takes place, by definition we have the following formula for the extent:

$$dn_k = \nu_k \, d\xi \tag{1.89}$$

1.9. Azeotropic transformations

A closed system undergoes an azeotropic transformation when, during the course of the transformation, the masses of some of the phases increase at the expense of others, without a change in the composition of the phases. This is expressed, for all phases α and all compositions, by the property:

$$x_k^{(\alpha)} = x_k^{0(\alpha)} \tag{1.90}$$

$x_k^{0(\alpha)}$ denotes the molar fraction of component A_k in phase α at the initial time of the transformation and $x_k^{(\alpha)}$ its molar fraction at any given moment during the transformation.

By deriving equation [1.90] in relation to time, we find the following for any component A_k in any phase α:

$$\frac{dx_k^{(\alpha)}}{dt} = 0 \tag{1.91}$$

In view of the definition of the molar fractions, this relation is written as:

$$\frac{dn_k^{(\alpha)}}{dt} - x_k^{0(\alpha)} \sum_{i=1}^{N} \frac{dn_i^{(\alpha)}}{dt} = 0 \tag{1.92}$$

We can apply this condition to a system with only one transformation with the fractional extent ξ. We then obtain:

$$\frac{d\xi}{dt} = x_k^{0(\alpha)} \frac{d\xi}{dt} \sum_{i=1}^{N} v_i^{(\alpha)} = 0 \qquad [1.93]$$

or:

$$x_k^{0(\alpha)} = \frac{v_k^{(\alpha)}}{\sum_{i=1}^{N} v_i^{\alpha}} \qquad [1.94]$$

At the initial time, all of the components must be in stoichiometric proportions in each phase.

Another case encountered when we look at phase-change in multi-component systems is when each component is involved in only one transformation, and its stoichiometric number is 1. Thus, in a phase α, we have:

$$\frac{d\xi_k^{(\alpha)}}{dt} = x_k^{0(\alpha)} \sum_{i=1}^{N} v_i \frac{d\xi_i^{(\alpha)}}{dt} \qquad [1.95]$$

This can also be written as:

$$\frac{\dfrac{d\xi_i^{(\alpha)}}{dt}}{\dfrac{d\xi_k^{(\alpha)}}{dt}} = \frac{x_i^{0(\alpha)}}{x_k^{0(\alpha)}} \qquad [1.96]$$

This means that the transformation rates of two components are in a constant ratio to one another, with the value of that ratio being determined by the initial conditions.

In addition, if we consider two phases α and β, by applying relation [1.92] for component A_k in the two phases and adding together the expressions obtained, we find:

$$\frac{dn_k^{(\alpha)}}{dt} + \frac{dn_k^{(\beta)}}{dt} - x_k^{0(\alpha)} \sum_{i=1}^{N} \frac{dn_i^{(\alpha)}}{dt} - x_k^{0(\beta)} \sum_{i=1}^{N} \frac{dn_i^{(\beta)}}{dt} = 0 \qquad [1.97]$$

However, as we are dealing with the case where there is only one transformation per component, we necessarily have stoichiometric numbers of 1:

$$\frac{dn_k^{(\alpha)}}{dt} = -\frac{dn_k^{(\beta)}}{dt} \qquad [1.98]$$

and:

$$\sum_{i=1}^{N} \frac{dn_i^{(\alpha)}}{dt} = -\sum_{i=1}^{N} \frac{dn_i^{(\beta)}}{dt} \qquad [1.99]$$

Finally, we deduce from this:

$$x_k^{0(\alpha)} = x_k^{0(\beta)} \qquad [1.100]$$

In the initial state, the molar fractions are the same in both phases.

Thus, the necessary and sufficient conditions for a phase change to be an azeotropic transformation are that:

– the system starts in an equi-content initial state;

– the ratio of the transfer rates is constant over time.

NOTE 1.5.– The azeotropic nature of the transformation pertains only to the compositions of the phases; it is independent of the external intensive variables (temperature, pressure, etc.) insofar as the azeotropic nature of the process only covers the compositions of phases; it is not dependent on external intensive variables (temperature, pressure, etc.), because all the kinetic laws of transition from one phase to another are identical functions of these variables.

The results in this section never entail the hypothesis that the transformations are at equilibrium; they are just as applicable for true transformations as for reversible transformations. In the latter case, the rates are null, and we are left with the condition of equi-content [1.100].

An example of azeotropic transformations, besides certain phase changes, includes the transformation:

$$\{\{HCl\}\} + \{\{NH_3\}\} = < NH_4Cl > \qquad [1R.4]$$

If we start with the three components, the gaseous phase is equimolecular in ammonia and hydrogen chloride.

Another example is given by the decomposition of calcium carbonate:

$$< \text{Ca CO}_3 > = < \text{CaO} > + \{ \text{CO}_2 \} \qquad\qquad\qquad [1R.5]$$

If, at the initial time, we begin with a mixture of the three components in arbitrary proportions because they belong to different phases, the transformation is always azeotropic.