Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

A Theory of Chemical Separations: Partition States

Peter R. Rony[a]
[a] Central Research Department, Monsanto Company Saint Louis, Missouri

To cite this Article Rony, Peter R.(1969) 'A Theory of Chemical Separations: Partition States', Separation Science and Technology, 4: 5, 413 — 423

To link to this Article: DOI: 10.1080/01496396908052267

URL: http://dx.doi.org/10.1080/01496396908052267

SEPARATION SCIENCE, 4(5), pp. 413–423, October, 1969

A Theory of Chemical Separations: Partition States

PETER R. RONY
CENTRAL RESEARCH DEPARTMENT
MONSANTO COMPANY
SAINT LOUIS, MISSOURI 63166

Summary

The fundamental chemical entity in any equilibrium chemical system is the *partition state*, which is the state formed by the reversible physical or chemical reaction between a component i and an environment s. Such a state represents a unifying concept for the description of partitioning chemical systems, phase equilibria, and chemical equilibria. It is defined thermodynamically and applied to a chemical system containing five different components and three chemical equilibria.

INTRODUCTION

It has been previously proposed that the fundamental chemical entity in an equilibrium chemical system is the chemical state formed by the reversible physical or chemical reaction between a component i and an environment s (*1*). This state is called a *partition state* and is designated by the notation $\boxed{i{:}s}$. When the environment s is a chemical environment, the colon represents a chemical bond of any bond energy, whereas when s is a physical environment, the colon has no clear physical identity. Although a partition state can be a discrete chemical entity, such as a sugar-borate ionic complex (*1*), it most frequently is simply a dissolved, adsorbed, or gaseous molecule.

In the early stages of the development of the present theory of chemical separations, the concept of a partition state was invented purely as a matter of convenience to facilitate both the mathematical derivation and the physical interpretation of the final theoretical results (*1*). With time, however, it assumed greater importance until, at present, it appears to be a useful unifying concept for the description of partitioning chemical systems, phase equilibria, and chemical equilibria. In order to understand its fundamental role in partitioning chemical systems, we would like to present a thermodynamic justification for the concept of a partition state. The reader is directed to a very useful text by Prigogine and Defay (*2*), whose treatment has been followed and extended in the present discussion.

DEFINITIONS

We will first define the terms reaction, chemical reaction, physical reaction, chemical equilibrium, and physical equilibrium, since they will be used repeatedly throughout the discussion. Prausnitz stated in his course notes on the theory of phase equilibria that:

> The word reaction, taken in its broadest sense, means any change in the internal constitution of the system. Such a change may be in the physical state of the components or the result of chemical transformations among the molecules in the system (*3*).

This definition will be followed with only slight additions: the change in the "physical state of the components" will be called a *physical reaction* and a "chemical transformation among the molecules" will be called a *chemical reaction.*

When applied to chemical systems, the term equilibrium has in the past been used in two ways: (1) to denote the *condition* of equilibrium, where the chemical affinities of all reactions are equal to zero, and (2) to collectively denote two or more physical or chemical *reactions* whose affinities are equal to zero, i.e., phase equilibria or chemical equilibria. We will follow the second of these meanings and make the following definitions: a *chemical equilibrium* is a chemical reaction in which the chemical affinity is equal to zero; a *physical equilibrium* is a physical reaction in which the chemical affinity is equal to zero. Instead of phase equilibria, a term freqently found in the literature, we are thus using the term physical equilibria, which means essentially the same thing.

THEORETICAL

At constant temperature and pressure, the *condition* of equilibrium stated above can be expressed very simply in terms of chemical potentials,

$$\sum_i \nu_i \mu_i = 0 \qquad \text{at equilibrium,} \tag{1}$$

where ν_i and μ_i are the stoichiometric coefficient and chemical potential, respectively, for component i in a *single* reaction, whether physical or chemical (*2*). Three examples are: (1) the equilibrium combustion of methane,

$$CH_4 + 2O_2 \rightleftharpoons CO_2 + 2H_2O$$

where the condition of *chemical* equilibrium is

$$\mu_{CH_4} + 2\mu_{O_2} = \mu_{CO_2} + 2\mu_{H_2O} \tag{2}$$

(2) the equilibrium distribution of a component i between phases 1 and 2,

$$i \text{ (in 1)} \rightleftharpoons i \text{ (in 2)}$$

where the condition of *physical* equilibrium is

$$\mu_{i1} = \mu_{i2} \tag{3}$$

and (3) the equilibrium distribution of a component i between phases 1 and 2 and the simultaneous equilibrium chemical reaction with a molecule M in phase 1,

$$\begin{array}{l} i \text{ (in 1)} \rightleftharpoons i \text{ (in 2)} \\ + \\ \mathrm{M} \\ \upharpoonleft\!\downharpoonright \\ i{:}\mathrm{M} \text{ (complex dissolved in 1)} \end{array}$$

for which the *two* conditions of physical and chemical equilibrium are

$$\mu_{i1} = \mu_{i2} \tag{4}$$

$$\mu_{i1} + \mu_M = \mu_{i:M} \tag{5}$$

When we are only interested in the behavior of component i (and the nature and amount of M is relatively unimportant), it would be useful if the condition of equilibrium in example (3) could be simply stated as

$$\mu_{i1} = \mu_{i2} = \mu_{i:M} \tag{6}$$

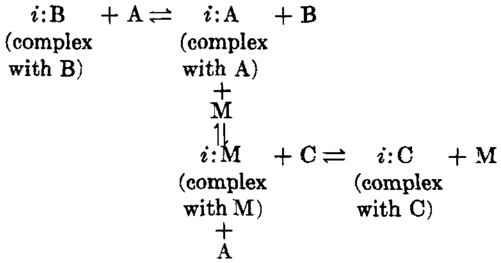
Unfortunately, such an equality is clearly impossible according to Eq. (5). Can we do anything about the μ_M term in Eq. (5)? Yes, we can define a "new" chemical potential, $\mu'_{i:M}$,

$$\mu'_{i:M} = \mu_{i:M} - \mu_M \tag{7}$$

to obtain the desired relationship

$$\mu_{i1} = \mu_{i2} = \mu'_{i:\mathrm{M}} \tag{8}$$

In this example, we have employed i (in 1) as a "reference state." Since it is not obvious why we did this, let us consider a more complicated set of equilibrium reactions where the use of a "reference state" can be seen more clearly:



The three independent conditions of chemical equilibrium are

$$\mu_{i:\mathrm{B}} + \mu_{\mathrm{A}} = \mu_{i:\mathrm{A}} + \mu_{\mathrm{B}} \tag{9}$$

$$\mu_{i:\mathrm{A}} + \mu_{\mathrm{M}} = \mu_{i:\mathrm{M}} + \mu_{\mathrm{A}} \tag{10}$$

$$\mu_{i:\mathrm{M}} + \mu_{\mathrm{C}} = \mu_{i:\mathrm{C}} + \mu_{\mathrm{M}} \tag{11}$$

Let us choose i:A as a "reference state" and recast these equations in the following way:

$$\mu_{i:\mathrm{A}} = \mu_{i:\mathrm{B}} + \mu_{\mathrm{A}} - \mu_{\mathrm{B}} \tag{12}$$

$$\mu_{i:\mathrm{A}} = \mu_{i:\mathrm{M}} + \mu_{\mathrm{A}} - \mu_{\mathrm{M}} \tag{13}$$

$$\mu_{i:\mathrm{A}} = \mu_{i:\mathrm{C}} + \mu_{\mathrm{A}} - \mu_{\mathrm{C}} \tag{14}$$

(We have combined Eqs. (10) and (11) to obtain Eq. (14).) If we now define three "new" chemical potentials,

$$\mu'_{i:\mathrm{B}} = \mu_{i:\mathrm{B}} + \mu_{\mathrm{A}} - \mu_{\mathrm{B}} \tag{15}$$

$$\mu'_{i:\mathrm{M}} = \mu_{i:\mathrm{M}} + \mu_{\mathrm{A}} - \mu_{\mathrm{M}} \tag{16}$$

$$\mu'_{i:\mathrm{C}} = \mu_{i:\mathrm{C}} + \mu_{\mathrm{A}} - \mu_{\mathrm{C}} \tag{17}$$

and substitute them into the above equations, we obtain a result analogous to Eq. (8),

$$\mu_{i:\mathrm{A}} = \mu'_{i:\mathrm{B}} = \mu'_{i:\mathrm{C}} = \mu'_{i:\mathrm{M}} \tag{18}$$

Clearly, a reference state must be chosen before we can unambiguously define these "new" chemical potentials. If we select i:B as the reference state, we will obtain a different set of "new" chemical potentials,

$$\mu_{i:\mathrm{B}} = \mu''_{i:\mathrm{A}} = \mu''_{i:\mathrm{C}} = \mu''_{i:\mathrm{M}} \tag{19}$$

Fortunately, it doesn't matter which state is picked as the reference. Once such a state has been selected, the system is uniquely defined.

To illustrate these points, let us consider a system in which the chemical potentials of the components are all of the form,

$$\mu_i \equiv \mu_i^{\dagger} + RT \ln a_i \tag{20}$$

where a_i is the activity of component i. By substituting Eq. (20) into Eq. 1, we obtain

$$\sum_i \nu_i \mu_i = \sum_i \nu_i \mu_i^{\dagger} + RT \sum_i \nu_i \ln a_i = 0 \tag{21}$$

With the aid of Prigogine and Defay's definition for the equilibrium constant, $\mathbf{K}(T,P)$, of a reaction (*2*),

$$RT \ln \mathbf{K}(T,P) \equiv - \sum_i \nu_i \mu_i^{\dagger} \tag{22}$$

Eq. (21) can be simplified to

$$\mathbf{K}(T,P) = \prod_i a_i^{\nu_i} \tag{23}$$

We can also define the activity coefficient, γ_i, by

$$\gamma_i \equiv \frac{a_i}{X_i} \tag{24}$$

where X_i is the mole fraction of component i, and convert Eq. (23) to

$$\mathbf{K}(T,P) = \prod_i \gamma_i^{\nu_i} \prod_i X_i^{\nu_i} \tag{25}$$

If the system is ideal, the relationship

$$\prod_i \gamma_i^{\nu_i} = 1 \qquad \text{ideal system} \tag{26}$$

holds and Eq. (25) simplifies to

$$\mathbf{K}(T,P) = \prod X_i^{\nu_i} \qquad \text{ideal system} \tag{27}$$

for *each physical or chemical reaction.*

When we substitute Eq. (20) into Eq. (18), we obtain

$$\mu^{\dagger}_{i:\mathrm{A}} + RT\ln a_{i:\mathrm{A}} = \mu^{\dagger}_{i:\mathrm{B}} + \mu^{\dagger}_{\mathrm{A}} - \mu^{\dagger}_{\mathrm{B}} + RT\ln\frac{a_{i:\mathrm{B}}a_{\mathrm{A}}}{a_{\mathrm{B}}} \tag{28}$$

$$\mu^{\dagger}_{i:\mathrm{A}} + RT\ln a_{i:\mathrm{A}} = \mu^{\dagger}_{i:\mathrm{C}} + \mu^{\dagger}_{\mathrm{A}} - \mu^{\dagger}_{\mathrm{C}} + RT\ln\frac{a_{i:\mathrm{C}}a_{\mathrm{A}}}{a_{\mathrm{C}}} \tag{29}$$

$$\mu^{\dagger}_{i:\mathrm{A}} + RT\ln a_{i:\mathrm{A}} = \mu^{\dagger}_{i:\mathrm{M}} + \mu^{\dagger}_{\mathrm{A}} - \mu^{\dagger}_{\mathrm{M}} + RT\ln\frac{a_{i:\mathrm{M}}a_{\mathrm{A}}}{a_{\mathrm{M}}} \tag{30}$$

These equations can be further simplified to

$$\frac{a_{i:\mathrm{B}}}{a_{i:\mathrm{A}}} = \mathbf{K}_{\mathrm{B}}\frac{a_{\mathrm{B}}}{a_{\mathrm{A}}} \tag{31}$$

$$\frac{a_{i:\mathrm{C}}}{a_{i:\mathrm{A}}} = \mathbf{K}_{\mathrm{C}}\frac{a_{\mathrm{C}}}{a_{\mathrm{A}}} \tag{32}$$

$$\frac{a_{i:\mathrm{M}}}{a_{i:\mathrm{A}}} = \mathbf{K}_{\mathrm{M}}\frac{a_{\mathrm{M}}}{a_{\mathrm{A}}} \tag{33}$$

if the equilibrium constants $\mathbf{K}_{\mathrm{B}}$, $\mathbf{K}_{\mathrm{C}}$, and $\mathbf{K}_{\mathrm{M}}$ are defined as

$$\mathbf{K}_{\mathrm{B}} = \exp\left[\frac{\mu^{\dagger}_{i:\mathrm{A}} + \mu^{\dagger}_{\mathrm{B}} - \mu^{\dagger}_{i:\mathrm{B}} - \mu^{\dagger}_{\mathrm{A}}}{RT}\right] \tag{34}$$

$$\mathbf{K}_{\mathrm{C}} = \exp\left[\frac{\mu^{\dagger}_{i:\mathrm{A}} + \mu^{\dagger}_{\mathrm{C}} - \mu^{\dagger}_{i:\mathrm{C}} - \mu^{\dagger}_{\mathrm{A}}}{RT}\right] \tag{35}$$

$$\mathbf{K}_{\mathrm{M}} = \exp\left[\frac{\mu^{\dagger}_{i:\mathrm{A}} + \mu^{\dagger}_{\mathrm{M}} - \mu^{\dagger}_{i:\mathrm{M}} - \mu^{\dagger}_{\mathrm{A}}}{RT}\right] \tag{36}$$

When we perform this same type of analysis on the equations that lead to Eq. (19), we obtain

$$\frac{a_{i:\mathrm{A}}}{a_{i:\mathrm{B}}} = \frac{1}{\mathbf{K}_{\mathrm{B}}}\frac{a_{\mathrm{A}}}{a_{\mathrm{B}}} \tag{37}$$

$$\frac{a_{i:\mathrm{C}}}{a_{i:\mathrm{B}}} = \frac{\mathbf{K}_{\mathrm{C}}}{\mathbf{K}_{\mathrm{B}}}\frac{a_{\mathrm{C}}}{a_{\mathrm{B}}} \tag{38}$$

$$\frac{a_{i:\mathrm{M}}}{a_{i:\mathrm{B}}} = \frac{\mathbf{K}_{\mathrm{M}}}{\mathbf{K}_{\mathrm{B}}}\frac{a_{\mathrm{M}}}{a_{\mathrm{B}}} \tag{39}$$

Clearly, the same result is obtained no matter whether $i{:}\mathrm{A}$, $i{:}\mathrm{B}$, $i{:}\mathrm{C}$, or $i{:}\mathrm{M}$ is chosen as the reference state. In addition, there are only three independent equilibrium constants. The fourth equilibrium constant, that for the reference state, is identically equal to one,

$$\frac{a_{i:\mathrm{A}}}{a_{i:\mathrm{A}}} = \mathbf{K}_{\mathrm{A}}\frac{a_{\mathrm{A}}}{a_{\mathrm{A}}} \equiv 1. \tag{40}$$

PHYSICAL SIGNIFICANCE OF THE PARTITION STATE

We are now in a position to discuss the physical significance of the "new" chemical potentials and their relationship to partition states. The condition for *phase equilibrium* in a multiphase multicomponent chemical system can be stated in a very simple and precise way. For example:

> If two phases are in equilibrium, all components capable of passing from one to the other must have the same chemical potential in the two phases (*2*);
>
> The value of the fugacity of any component is the same in all phases in equilibrium (*4*);
>
> The partial free energy (or chemical potential) of each component in one phase is equal to its partial free energy in the other phases (*5*).

In most texts on thermodynamics, no similar statement for the condition of chemical equilibrium is ever made. Yet, we might intuitively expect that, if we would replace the word "phase" by a more appropriate term, we should be able to make statements that are independent of the adjectives "phase" and "chemical," such as:

> If two ——— are in equilibrium, all components capable of passing from one to the other must have the same chemical potential in the two ———; or
>
> The value of the fugacity of any component is the same in all ——— in equilibrium; or
>
> The partial free energy (or chemical potential) of each component in one ——— is equal to its partial free energy in the other ———.

Hopefully, a term ——— could be found such that the distinction between phase and chemical equilibria would no longer be necessary. From Eqs. (8), (18), and (19), which are rigorously correct from a thermodynamic standpoint, it is clear that we can make such statements. The only task left is to decide what the term ——— means and how it and the "new" chemical potentials are related.

If the components A, B, C, and M are omitted from the representation, the reactions that correspond to Eq. (18) can be written as

$$\underset{\substack{\text{(complex}\\\text{with B)}}}{i\text{:B}} \rightleftharpoons \underset{\substack{\text{(complex}\\\text{with A)}}}{i\text{:A}} \rightleftharpoons \underset{\substack{\text{(complex}\\\text{with M)}}}{i\text{:M}} \rightleftharpoons \underset{\substack{\text{(complex}\\\text{with C)}}}{i\text{:C}}$$

If A, B, C, and M are all environments, then, according to a definition given previously, $\boxed{i\text{:A}}$, $\boxed{i\text{:B}}$, $\boxed{i\text{:C}}$, $\boxed{i\text{:M}}$ are all *partition states* (from this point forward, a box will be used to identify a partition state). The above reaction can thus be represented as the successive equilibration of component i among a series of partition states,

$$\begin{array}{ccccccc} \boxed{i\text{:B}} & \rightleftharpoons & \boxed{i\text{:A}} & \rightleftharpoons & \boxed{i\text{:M}} & \rightleftharpoons & \boxed{i\text{:C}} \\ \text{(complex} & & \text{(complex} & & \text{(complex} & & \text{(complex} \\ \text{with B)} & & \text{with A)} & & \text{with M)} & & \text{with C)} \end{array}$$

With $\boxed{i\text{:A}}$ as a reference partition state, Eqs. (15) to (17) *define* the chemical potentials of these partition states. Thus,

$$\begin{array}{lccccccc} & \boxed{i\text{:B}} & \rightleftharpoons & \boxed{i\text{:A}} & \rightleftharpoons & \boxed{i\text{:M}} & \rightleftharpoons & \boxed{i\text{:C}} \\ \text{Chemical} & & & & & & & \\ \text{potentials:} & \mu'_{i:\mathrm{B}} & = & \mu_{i:\mathrm{A}} & = & \mu'_{i:\mathrm{M}} & = & \mu'_{i:\mathrm{C}} \\ & & & \text{(reference)} & & & & \\ & \text{Eq. (15)} & & \text{—} & & \text{Eq. (16)} & & \text{Eq. (17).} \end{array}$$

Clearly, the "new" chemical potentials, $\mu'_{i:\mathrm{B}}$, $\mu'_{i:\mathrm{C}}$, and $\mu'_{i:\mathrm{M}}$, are simply the chemical potentials of $\boxed{i\text{:B}}$, $\boxed{i\text{:C}}$, and $\boxed{i\text{:M}}$, and the term ——— represents the word, *partition state.*

We can now define the condition of equilibrium in a multiphase multicomponent system as:

> At thermodynamic equilibrium, the chemical affinity for each physical or chemical reaction is equal to zero; or
>
> At thermodynamic equilibrium, the value of the fugacity of component i, with respect to a given reference partition state, is the same in all partition states; or
>
> At thermodynamic equilibrium, the value of the chemical potential of component i, with respect to a given reference partition state, is the same in all partition states.

The partition state is therefore a useful concept even in equilibrium thermodynamic systems. It bridges the gap between phase and chemical equilibria by not making a distinction between the two, i.e., by not making a distinction between a molecule that dissolves and one that participates in a chemical reaction.

PARTITION COEFFICIENT

When the environments are in great excess of component i, the chemical potential of i can be expressed in terms of its molar concentration, c_i,

$$\mu_i \equiv \mu_i^\ddagger + RT \ln \gamma_i c_i \qquad (41)$$

where $\mu_i^\ddagger$ has a value different from $\mu_i^\dagger$ but γ_i is identical to the activity coefficient given in Eq. (24) (*2*). A new equilibrium constant, $\mathbf{K}^\ddagger(T,P)$, must also be defined,

$$RT \ln \mathbf{K}^\ddagger(T,P) \equiv -\sum_i \nu_i \mu_i^\ddagger \qquad (42)$$

where $\mathbf{K}^\ddagger(T,P)$ now has concentration units and a magnitude different from $\mathbf{K}(T,P)$. The equation corresponding to Eq. (25) is

$$\mathbf{K}^\ddagger(T,P) = \prod_i \gamma_i^{\nu_i} \prod_i c_i^{\nu_i} \qquad (43)$$

which simplifies to

$$\mathbf{K}^\ddagger(T,P) = \prod_i c_i^{\nu_i} \qquad \text{ideal system} \qquad (44)$$

for a *single* physical or chemical reaction in an ideal system.

Using this new equilibrium constant, we can convert Eqs. (31) to (33) to

$$\frac{c_{i:\mathrm{B}}}{c_{i:\mathrm{A}}} = \mathbf{K}_\mathrm{B}^\ddagger \frac{c_\mathrm{B}}{c_\mathrm{A}} \frac{\gamma_\mathrm{B}\gamma_{i:\mathrm{A}}}{\gamma_\mathrm{A}\gamma_{i:\mathrm{B}}} = \kappa_{i:\mathrm{B}} \qquad (45)$$

$$\frac{c_{i:\mathrm{C}}}{c_{i:\mathrm{A}}} = \mathbf{K}_\mathrm{C}^\ddagger \frac{c_\mathrm{C}}{c_\mathrm{A}} \frac{\gamma_\mathrm{C}\gamma_{i:\mathrm{A}}}{\gamma_\mathrm{A}\gamma_{i:\mathrm{C}}} = \kappa_{i:\mathrm{C}} \qquad (46)$$

$$\frac{c_{i:\mathrm{M}}}{c_{i:\mathrm{A}}} = \mathbf{K}_\mathrm{M}^\ddagger \frac{c_\mathrm{M}}{c_\mathrm{A}} \frac{\gamma_\mathrm{M}\gamma_{i:\mathrm{A}}}{\gamma_\mathrm{A}\gamma_{i:\mathrm{M}}} = \kappa_{i:\mathrm{M}} \qquad (47)$$

where $\kappa_{i:\mathrm{B}}$, $\kappa_{i:\mathrm{C}}$, and $\kappa_{i:\mathrm{M}}$, the *partition coefficients* of $\boxed{i{:}\mathrm{B}}$, $\boxed{i{:}\mathrm{C}}$, and $\boxed{i{:}\mathrm{M}}$, are written with respect to reference state $\boxed{i{:}\mathrm{A}}$, as can be seen from Eq. (48),

$$\frac{c_{i:\mathrm{A}}}{c_{i:\mathrm{A}}} = \kappa_{i:\mathrm{A}} = 1 \qquad (48)$$

List of Symbols

a	activity
c	concentration (moles/cm^3)
$\mathbf{K}$	thermodynamic equilibrium constant defined by Eq. (23)
$\mathbf{K}^{\ddagger}$	thermodynamic equilibrium constant defined by Eq. (44)
P	total pressure (atm)
R	gas constant (1.987 Gibbs/mole)
T	temperature (°K)
X	mole fraction

Greek Letters

γ	activity coefficient
κ	partition coefficient (moles/cm^3:moles/cm^3)
μ	chemical potential (kcal/mole)
$\mu^{\dagger}$	standard state chemical potential defined by Eq. (20) (kcal/mole)
$\mu^{\ddagger}$	standard state chemical potential defined by Eq. (41) (kcal/mole)
μ'	chemical potential for a partition state (kcal/mole)
μ''	chemical potential for a partition state (kcal/mole)
ν	stoichiometric coefficient

Subscripts

i	component i
is	component i in environment s (i.e., partition state $\boxed{i:s}$)
s	environment s
A, B, C, M, CH_4, CO_2, O_2, H_2O	specific components
$i1$, $i2$, i:A, i:B, i:C, i:M	specific partition states

REFERENCES

1. P. R. Rony, *Separation Sci.*, **3**, 425 (1968). The quantity c_{is} has been inadvertently omitted from both sides of Eq. (13).
2. I. Prigogine and R. Defay, *Chemical Thermodynamics*, Longmans, London, 1954.
3. J. M. Prausnitz, *The Thermodynamic Theory of Phase Equilibria* (lecture notes), University of California, Berkeley, 1961.
4. E. D. Oliver, *Diffusional Separation Processes*, Wiley, New York, 1966, p. 12.
5. J. Coull and E. B. Stuart, *Equilibrium Thermodynamics*, Wiley, New York, 1964, p. 259.

Received by editor June 12, 1969