OSMOTIC PRESSURE AND VARIANCE

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I. *The Problem*

Components. The starting point of Gibbs's thermodynamic theory of chemical equilibrium is the differential equation¹

$$d\varepsilon = td\eta - pdv + \mu_1 dm_1 + \mu_2 dm_2 + \dots + \mu_\nu dm_\nu$$

expressing the relation holding among the differentials of the energy, entropy, volume, and masses of the several components of a «phase» of its substances. The ν components can be chosen in any way compatible with the condition that the differentials of their masses shall be independent and shall express every possible variation in the composition of the phase.² Gibbs shows further² that when h relations subsist among the units of these components, the number of «independently variable components» of the phase is

$$n = \nu - h, \quad (1)$$

and that the same is true of any system of phases taken as a whole.

This matter of the relation between the *components* and the *independently variable components* of a system has been put very clearly and completely by Gibbs,³ but in so abstract a manner that its signification can be well comprehended only by readers gifted with imagination and trained into a thoroughgoing familiarity with the pertinent facts. Bancroft has accordingly done an important service⁴ in lucidly stating the relation and in giving it illustration by all manner of application to material systems of various types. It has also been clearly and correctly employed in special cases in the thermodynamic studies of Duhem.⁵

¹Gibbs, Trans. Conn. Acad. **3**, 116 (1875).

²l. c. 117.

³l. c. pages 120 and thereafter.

⁴Bancroft, The Phase Rule, 227 (1897).

⁵Duhem, Dissolutions et mélanges, Trav. et mém. des fac. de Lille.

Osmotic Systems. The gain in practical comprehension so made led Bancroft one step further¹ to the very interesting conclusion that since the introduction of osmotic walls into a material system may increase the number of pressures there, the $n + 2$ variables in Gibbs's formulation for the number of degrees of freedom or the *variance* of the system²

$$v = n + 2 - r$$

are thereby increased to $n + 2 + a$, when the addition of osmotic walls introduces a new pressures.³ He thus recognized that the variance of a system containing osmotic pressures is changed in a perfectly definite manner by the appearance of these pressures.⁴

An advance in this direction is very important, for it lightens the difficulties hitherto attendant upon treating the osmotic phenomena in their proper connection with the simpler types of equilibrium with which they are allied—it is a step toward a more comprehensive classification by variance than has hitherto been possible. But upon closer examination of the matter in its present state one readily sees that the subject requires treatment in a more general way, for through the introduction of osmotic walls into a material system the $n + 2$ Gibbsian variables are, in the general case, increased by the

¹Bancroft. l. c. 235.

²Gibbs. l. c. 153 (1876).

³Gibbs. l. c. 138.

⁴The terminology of Variance used here has been employed by the writer for some years in all matters relating to a classification of material systems according to the number of their degrees of thermodynamic freedom (see this Journal, I, 167, and also Bancroft, Phase Rule, pp. 3 and 4). According to it all $(n + 2)$ -phase systems of the ordinary phase rule are nonvariant systems, all $(n + 1)$ -phase systems are monovariant ones, all n -phase systems are divariants, $(n - 1)$ -phase systems are trivariants, and so on; one may also refer to systems of variance greater than unity as polyvariants, which is often convenient.

A pure liquid with its saturated vapor constitutes therefore a one-component monovariant system, an unsaturated solution with vapor is a two-component divariant, a mixture of two gases is a trivariant, and so on. It is shown in this paper that in osmotic systems the variance is not necessarily

$$v = n + 2 - r,$$

and it is readily seen also that the same is true of many voltaic combinations.

appearance of new potentials as well as by that of new pressures.¹ The manner in which this circumstance must be taken into account shall now be considered.

II. The Generalized Phase Rule

1. *No Osmotic Walls.* To find the number of degrees of freedom of the thermodynamic behavior of a system, from the number of its independently variable components and that of its phases, Gibbs considers the differential equation for the energy of any one phase

$$d\varepsilon = td\eta - pdv + \sum_i^r \mu_i dm_i; \quad (2)$$

integrating this, over a change in the quantity of substance from zero to the given finite amount, at constant state (of temperature, pressure and composition),

$$\varepsilon = t\eta - pv + \sum_i^r \mu_i m_i, \quad (3)$$

and then differentiating for the likewise perfectly general expression

$$\begin{aligned} d\varepsilon = td\eta - pdv + \sum_i^r \mu_i dm_i \\ + \eta dt - v dp + \sum_i^r m_i d\mu_i, \end{aligned} \quad (4)$$

which in combination with (2) gives

$$0 = \eta dt - v dp + \sum_i^r m_i d\mu_i, \quad (5)$$

indicating that there exists for each phase a relation

$$f(t, p, \mu_1, \mu_2, \dots, \mu_r) \quad (6)$$

which is easily shown to be «fundamental» in Gibbs's sense. The variables appearing in (6) maintain uniform values throughout a system of r coexistent phases, and h relations obtain among the r potentials, so [equation (1)]

$$(r - h) + 2 = n + 2$$

variables remain independent for each phase and they are subject to r conditions—to as many conditions as there are equations among

¹Gibbs, l. c. 138

them. The number of degrees of freedom or the variance of the system is therefore

$$v = n + 2 - r. \quad (7)$$

2. *One Wall and No Separation.* In the cases thus treated by Gibbs there are however no osmotic pressures, the proof supposes the equilibrium pressures to have the same values at all coexistent phases. A simple case where this is no longer true is afforded by a two-component system of solvent and solute, separated into two portions by an osmotic wall permeable only for the solvent. These separated portions must now be regarded as individual phases, which involves a slight extension of Gibbs's definition. The attraction between the solute and the solvent will then establish an osmotic pressure upon one side of the wall, which will necessarily differ from the equilibrium pressure upon the other; the fundamental equations for the r phases of the system will then become—denoting by I the phases on the osmotic side of the wall, by II those on the other and by subscript l and s the solvent and solute respectively¹—

$$\left. \begin{aligned} f_I^1(t, p_I, \mu_{(s)}, \mu_{(l)}, \dots, \mu_n) &= 0 \\ f_I^2(t, p_I, \mu_{(s)}, \mu_{(l)}, \dots, \mu_n) &= 0 \\ \dots &\dots \\ f_I^{r-1}(t, p_I, \mu_{(s)}, \dots, \mu_n) &= 0 \\ f_{II}^r(t, p_{II}, \mu_{(s)}, \dots, \mu_n) &= 0. \end{aligned} \right\}$$

It is here supposed, for the sake of simplicity, that the h extra components have already been eliminated. There are in these equations n potentials, one temperature and two pressures, $n + 3$ variables in all and r relations holding among them, so the variance of the system is

$$v = n + 3 - r. \quad (7a)$$

This formulation is the phase rule for systems of the type considered.

The result may be illustrated by a system made up of a salt in water on one side of the osmotic wall and pure water with its vapor on the other, each component may be supposed kept at constant

¹The l and s might relate to 'liquid' and 'salt'.

volume by a closely fitting piston. The attraction between the salt and the water will draw water into the solution compartment until the osmotic pressure so produced there will have attained a value dependent upon the concentration. The concentration can be varied at constant temperature and the pressures will vary with varying temperature, so the equilibrium of the system is a divariant one although it has three, or $n + 1$, phases¹. The addition of a new phase, as for example ice in the water compartment or solid salt in that of the solution², must diminish the variance by unity, and we readily see from the arrangement indicated by Fig. 1 that the con-

FIG. 1.

centration of the solution, and consequently the osmotic pressure, can not be varied at constant temperature,—such change can be due to the change of temperature only, the system is monovariant. This follows immediately from (7a), for $n = 2$ and $r = 4$ so that

$$\begin{aligned} v &= n + 3 - r \\ &= 1. \end{aligned}$$

With the appearance of ice this system would become nonvariant; with solution on one side and solvent on the other it would be tri-variant, and this appears also from the equation, which for $n = 2$ and $r = 2$ gives

$$\begin{aligned} v &= 2 + 3 - 2 \\ &= 3. \end{aligned}$$

¹Bancroft. Phase Rule, 235.

²The appearance, under ordinary circumstances, of a vapor phase on the side containing solution is excluded, because the pressure there is greater than the vapor pressure of the pure liquid.

3. *One Wall and One Separation.* The determination of variance in cases like those just cited is the matter elucidated by Bancroft, but we pass to the introduction of new potentials as well as of new pressures when we consider cases in which the substances for which the wall is impermeable are present in phases separated by the wall. Under such circumstances the fundamental equations of the phases are

$$\left. \begin{aligned} f'_I(t, p_I, \mu_{(s)I}, \mu_{(p)}, \dots, \mu_n) &= 0 \\ f''_I(t, p_I, \mu_{(s)I}, \mu_{(p)}, \dots, \mu_n) &= 0 \\ \dots \\ f'^{r-1}_{II}(t, p_{II}, \mu_{(s)II}, \mu_{(p)}, \dots, \mu_n) &= 0 \\ f'^r_{II}(t, p_{II}, \mu_{(s)II}, \mu_{(p)}, \dots, \mu_n) &= 0 \end{aligned} \right\}$$

There are here $n + r$ potentials, one temperature and two pressures, $n + 4$ variables in all and consequently a variance of

$$v = n + 4 - r. \quad (7b)$$

Suppose for example the four-phase system represented in Fig. 2

FIG. 2.

The two solutions will have in general different compositions and accordingly different potentials of their components, the concentration and pressure of the solution in II only can be varied at constant temperature, so the equilibrium is a divariant one; this follows from (7b), which for $n = 2$ and $r = 4$ becomes

$$\begin{aligned} v &= 2 + 4 - 4 \\ &= 2 \end{aligned}$$

as stated. The transfer to a monovariant system may be made

through the appearance of ice in the unsaturated solution, the system then assuming the monovariant equilibrium of a fusion curve. With the freezing of ice from the compartment I the two sides of the system would become identical and the influence of the osmotic wall upon the equilibrium phenomena would disappear. This circumstance is illustrated more simply by the appearance of salt in II, above, with increasing concentration there. We should then have, as in Fig. 3, the phases of solid salt identical and also

FIG. 3.

those of solution, so that the two masses of salt for example form one phase as truly as do individual crystals of the salt and the situation is in no wise altered if the volume be increased so as to permit the appearance of a second mass of the vapor phase. The solutions must eventually come to the same level through the influence of gravity; the pressures and potentials are the same on each side of the membrane and the variance is simply $n + 2 - r$ or $2 + 2 - 3$, a monovariance, just as if the membrane were not present. Such identity of phases and consequent disappearance of osmotic pressures must not be overlooked in variance problems where osmotic walls are concerned. A similar state of affairs appears when a solution with other possible phases is separated by like osmotic walls from two different compartments containing pure solvent, with or without vapor,—the outside compartments contain but a single set of phases and so but one osmotic wall comes really into the consideration. This may also be shown, if it be so desired, by writing out the fundamental equations for all the phases.

4. *Two Like Walls and One Separation.* An increased complexity is reached by the introduction of two osmotic walls into a system, we will first consider these walls to be impermeable for the same components. The set of fundamental equations for the phases

of such a system, when it is supposed that the outside compartment III contains no solute, are

$$\left. \begin{aligned} f'_I(t, p_I, \mu_{(s)I}, \mu_{(l)}, \dots \mu_n) &= 0 \\ f''_I(t, p_I, \mu_{(s)I}, \mu_{(l)}, \dots \mu_n) &= 0 \\ &\dots \\ f^{i-1}_{II}(t, p_{II}, \mu_{(s)II}, \mu_{(l)}, \dots \mu_n) &= 0 \\ f^i_{II}(t, p_{II}, \mu_{(s)II}, \mu_{(l)}, \dots \mu_n) &= 0 \\ &\dots \\ f^{r-1}_{III}(t, p_{III}, \mu_{(l)}, \dots \mu_n) &= 0 \\ f^r_{III}(t, p_{III}, \mu_{(l)}, \dots \mu_n) &= 0 \end{aligned} \right\}$$

There appear here $n - r + 2$ potentials, one temperature and three pressures, or $n + 5$ variables in all with the consequent variance of

$$v = n + 5 - r. \quad (7c)$$

The simple arrangement, under this head, which is represented in Fig 4, has one possibility of a variation of an equilibrium pressure

FIG. 4.

at constant temperature, namely by changing, directly or by additional pressure, the composition of the solution in I. The system is therefore divariant,—and this result follows from equation (7c), for with $n = 2$ and $r = 5$

$$\begin{aligned} v &= 2 + 5 - 5 \\ &= 2 \end{aligned}$$

a divariance. Changes of variance through the introduction or disappearance of phases, and simplification of the system by the appearance of identical phases upon both sides of a wall, are readily

foreseen. Further, addition of solute to the compartment III is seen at once to introduce a new potential into the system and therefore to raise its variance by unity for any same number of phases.

5. *Two Unlike Walls and No Separation.* It should not be omitted to indicate at this point that the considerations employed in the foregoing hold in unchanged wise when the osmotic walls which appear in a given system are permeable not for the same but for different components.

Raoult has shown¹ that walls of vulcanized rubber are permeable for ethyl ether but not for methyl alcohol, while such of swine's bladder are permeable for the alcohol but not for the ether. It is therefore possible, with the aid of these membranes, to construct osmotic systems in which a mixture of the two substances named shall be in equilibrium with each of the pure components,—as is indicated in Fig. 5. We have here to do with two potentials, one

FIG. 5.

temperature and three different equilibrium pressures, six variables in all with five phases, *i. e.* five relations holding among these variables; the variance is therefore $6 - 5 = 1$, a monovariance. The equilibrium pressures of the system can obviously not be varied isothermally, so changes with changing temperature alone arise for consideration, the equilibrium is actually a monovariant one.

6. *Two Unlike Walls and One Separation.* The formation of a solution in one of the outer compartments of the above system must increase the variance by unity, of course; the process would produce for example the arrangement of Fig. 6. Here are two alcohol potentials, one for ether, one temperature and three pressures to be considered; seven variables with five relations among them—a

¹Raoult, Zeit. phys. Chem. **17**, 737 (1895).

	Stops alcohol	Stops ether
<i>Vapor</i>		<i>Vapor</i>
(<i>Ether</i>)	(<i>Ether</i>)	
(<i>Alcohol</i>)	(<i>Alcohol</i>)	<i>Alcohol</i>
I	II	III

FIG. 6.

variance of two as was foretold. One observes readily that the state of the system can be varied in one way isothermally—by changing the concentration of the dissolved alcohol in I—and the temperature can be changed as well, the system is actually in a divariant state. Other variations, with the addition, abstraction or replacement of phases are readily imaginable.

7. *Complex Cases.* If, instead of adding a new phase of solid solvent or the like, one should carry out the allied process of adding yet another osmotic wall, impermeable for alcohol let us say, the very interesting case of Fig. 7 would arise. Here the state of affairs

	Stops alcohol	Stops alcohol	Stops ether
<i>Vapor</i>			<i>Vapor</i>
<i>Ether</i>	(<i>Ether</i>)	(<i>Ether</i>)	
	(<i>Alcohol</i>)	(<i>Alcohol</i>)	<i>Alcohol</i>
I	II	III	IV

FIG. 7.

is governed primarily by the fact that the mass of alcohol in II is kept constant there by the walls of the cell. This circumstance causes the establishment of a definite equilibrium with the pure solvent in I, for any given volume of II. The solution of ether in

alcohol in III, on the other hand, will come to equilibrium with the alcohol of IV, the resulting pressure in III depending upon the volume and the amount of ether there. When II and III are, finally, set in communication they must come to an equilibrium between themselves which can only be when the composition of the latter becomes equal to that of the former—for ether can pass from I to III (or the reverse) and the displaced alcohol in III can flow out into IV. The two solutions will yet stand under different pressures, because, although they seem to have the same composition, one of them is in equilibrium with ether and the other is so with alcohol. The resulting equilibrium of the entire system is governed by the relative mass of the alcohol in II, which can be varied at constant temperature, the entire system of pressures will vary of course also with the temperature so the system is a divariant one. That such is the result of the theory is shown by counting the variables,—one potential for ether, two for alcohol, one temperature and four different pressures,—eight variables and six phases, with a resulting variance of two as shown by the experimental examination.

In connection with such cases it is instructive to consider the similar arrangement in which the separating osmotic walls are all of the same kind and impermeable for one component, say the solute. Such a system is presented in Fig. 8. Here the concentra-

FIG. 8.

tions in II and in III are in general different, so these two compartments must stand under different pressures to be each in equilibrium with the solvent and the vapor. This too is compatible with equilibrium between II and III. For suppose $p_{III} > p_{II}$; then, for given volumes of each of these two phases, the attraction of the solute in II, S_{II} , for the pure solvent, plus the difference of the attractions

which the solute in III, S_{III} , has for the solvent in II and S_{II} has for that in III, are exactly counterbalanced by the attraction which S_{II} has for the solvent in IV. This is indicated by the medium, light and heavy arrows in the figure. The compartment II with its two membranes may in fact be regarded as constituting a single membrane impermeable for the solute, the attraction of this latter for the pure solvent is then the same—from III—in either direction and it is immaterial how the pressure changes in the interior of the membrane. In such treatment the volume and mass of solute in II need not be supposed constant, that is to say the osmotic pressure is independent of the nature of the membrane.¹ The total result would be altered in no wise if the two end compartments should be connected directly, thus forming in appearance as they do in fact but one phase each of pure liquid and of vapor.

It will be remarked that only combinations of two components have been discussed in the above illustrations, the application of theory to systems of more than two components would seem to offer no especial difficulty.

8. *The Generalized Phase Rule.* It is now desirable, after the general canvass which has been made of the field, to condense the above considerations into a rule for determining the variance of any given osmotic system from its osmotic peculiarities and the number of its components—into a logical extension of the phase rule. To do so we have merely to note that the variance is always the total number of variables which a system exhibits, diminished by the number, r , of its phases. The variables are n potentials, being at least one for each independently variable component, one for the temperature and one for at least one pressure, with x for the added pressures introduced by the appearance of x osmotic walls² and y for each of the y separations of a component by such a wall.

The total number of variables is therefore

$$n + 2 + x + y$$

and the variance is

¹Compare, in connection with this, van 't Hoff, Zeit. phys. Chem. **9**, 477 (1892).

²Save when a set of phases is simply reproduced and two pressures become equal.

$$v = n + 2 + x + y - r.$$

This is the generalized phase rule, as applicable to systems containing osmotic pressures. For the limiting case in which all osmotic walls are absent we have both $x = 0$ and $y = 0$ and consequently the Gibbsian variance of

$$v = n + 2 - r.$$

III. Test of the Rule

To test the correctness of this formulation and at the same time illustrate the convenience, the readiness, of its application let us apply it successively to the cases adduced in the foregoing section. Following the previous order and numbering we have, first, for single walls and no separations,

<i>Solution</i>	<i>Vapor</i>	(1)
<i>Salt</i>	<i>Solvent</i>	

one extra pressure and no separations, $n = 2$, $x = 1$, $y = 0$,

$$\begin{aligned} v &= 2 + 2 + 1 + 0 - 4 \\ &= 1, \end{aligned}$$

a monovariant ; then, when the solution is unsaturated,

<i>Solution</i>	<i>Vapor</i>	(1a)
	<i>Solvent</i>	

$$\begin{aligned} v &= 2 + 2 + 1 + 0 - 3 \\ &= 2, \end{aligned}$$

a divariant ; next, when the solvent freezes,

<i>Solution</i>	<i>Vapor</i>	(1b)
	<i>Ice</i>	
<i>Salt</i>	<i>Solvent</i>	

$$\begin{aligned} v &= 2 + 2 + 1 + 0 - 5 \\ &= 0, \end{aligned}$$

a nonvariant ; and finally when the solution and solvent are present alone,

<i>Solution</i>	<i>Solvent</i>	(1c)
$v = 2 + 2 + 1 + 0 - 2$		
$= 3,$		

the system is a trivariant. For single walls with one separation there were considered

<i>Solution</i>	<i>Vapor</i>	(2)
<i>Salt</i>	<i>Solution</i>	
$n = 2$	$x = 1$	
$y = 1$		
$v = 2 + 2 + 1 + 1 - 4$		
$= 2,$		

the system is divariant ; but in

<i>Solution</i>	<i>Vapor</i>	(2a)
<i>Salt</i>	<i>Ice</i>	
$n = 2$	$x = 1$	
$y = 1$		
$v = 2 + 2 + 1 + 1 - 5$		
$= 1,$		

it is monovariant. The system (3) introduced no new pressures and no separations, so we pass to (4) with two walls and one separation,

<i>Solution I</i>	<i>Solution II</i>	<i>Vapor</i>	(4)
<i>Salt</i>	<i>Salt</i>	<i>Solvent</i>	
$n = 2$	$x = 2$	$y = 1$	
$v = 2 + 2 + 2 + 1 - 5$	$= 2,$		

a divariant ; then the same with two separations,

<i>Solution I</i>	<i>Solution II</i>	<i>Vapor</i>	(4a)
<i>Salt</i>	<i>Salt</i>	<i>Solution III</i>	
$n = 2$	$x = 2$	$y = 2$	
$v = 2 + 2 + 2 + 2 - 5$	$= 3,$		

a trivariant. With two unlike walls and no separation we considered

$$\begin{array}{c}
 \left| \begin{array}{c} \text{Vapor} \\ \text{Ether} \end{array} \right| \left| \begin{array}{c} \text{Solution} \end{array} \right| \left| \begin{array}{c} \text{Vapor} \\ \text{Alcohol} \end{array} \right| \quad (5) \\
 n = 2 \qquad \qquad x = 2 \qquad \qquad y = 0 \\
 v = 2 + 2 + 2 + 0 - 5 \\
 = 1,
 \end{array}$$

a monovariant; and with one separation,

$$\begin{array}{c}
 \left| \begin{array}{c} \text{Vapor} \\ \text{Solution I} \end{array} \right| \left| \begin{array}{c} \text{Solution II} \end{array} \right| \left| \begin{array}{c} \text{Vapor} \\ \text{Alcohol} \end{array} \right| \quad (6) \\
 n = 2 \qquad \qquad x = 2 \qquad \qquad y = 1 \\
 v = 2 + 2 + 2 + 1 - 5 \\
 = 2,
 \end{array}$$

a divariant. For the "complex cases" we have

$$\begin{array}{c}
 \left| \begin{array}{c} \text{Vapor} \\ \text{Ether} \end{array} \right| \left| \begin{array}{c} \text{Solution II} \end{array} \right| \left| \begin{array}{c} \text{Solution III} \end{array} \right| \left| \begin{array}{c} \text{Vapor} \\ \text{Alcohol} \end{array} \right| \quad (7) \\
 n = 2 \qquad \qquad x = 3 \qquad \qquad y = 1 \\
 v = 2 + 2 + 3 + 1 - 6 \\
 = 2,
 \end{array}$$

the system is a divariant; and, finally, with like membranes we have the case

$$\left| \begin{array}{c} \text{Vapor} \\ \text{Solvent} \end{array} \right| \left| \begin{array}{c} \text{Solution II} \end{array} \right| \left| \begin{array}{c} \text{Solution III} \end{array} \right| \left| \begin{array}{c} \text{Vapor} \\ \text{Solvent} \end{array} \right| \quad (8)$$

The two end compartments here have been shown (as is indeed now apparent from inspection) to constitute but a single pair of phases, so that they might in fact be connected by a canal without disturbing the equilibrium; accordingly

$$\begin{array}{c}
 n = 2 \qquad \qquad x = 2 \qquad \qquad y = 1 \\
 v = 2 + 2 + 2 + 1 - 4 \\
 = 3,
 \end{array}$$

the system is trivariant. This is obviously true, for the equilibrium pressures can be varied in two ways isothermally, by changing the concentrations of either of the inside compartments.

The variance as thus determined accords in every case with that worked out in the preceding section. Any number of further combinations might be added, but it is believed that those given are sufficient for the present purpose. It may be well nevertheless to add, in closing, that two-component systems can be arranged with vapor alone or with vapor and ice in one of their compartments: Imagine for example the system depicted in Fig. 9; the solution, supposed

FIG. 9.

sufficiently concentrated, may be allowed to expand until it shall have absorbed entirely the relatively small amount of solvent in II, and it may then be brought into equilibrium with the unsaturated vapor of II by suitably altering the pressure. The consequent variance will be that conditioned by one extra pressure and no separation, namely

$$v = 2 + 2 + 1 + 0 - 2 \\ = 3,$$

a trivariance¹,—and it would be reduced to a divariance by cooling the system to the temperature at which ice appears in the vapor compartment. It is well worth while to reflect upon such cases when studying osmotic phenomena.

¹It will be noted that the pressure of the vapor will not in general be that of the saturated vapor of the solution as it stands.

IV. Close

The peculiar advantage accruing from definite determination of the variance of systems containing osmotic pressures is that the relations of the equilibria of such systems to those of the simpler types of thermodynamic equilibrium where osmotic pressures do not appear become thereby apparent. One may classify the equilibria with which physical chemistry is concerned in two ways, which offer, each of them, decided advantages; one can classify either primarily according to the variance and secondarily according to the number of independently variable components—thus treating all monovariant systems together, then all divariants and so on—or classify primarily according to the number of independently variable components and secondarily according to the variance. When following the latter plan one completes the discussion of one-component systems before attacking that of two-component systems; and under the head of two-component systems one can begin the treatment of osmotic phenomena, and discuss them in the order of the variance of the equilibria in hand. The whole scheme of presentation becomes thereby very orderly and coherent, and it has for these reasons much to recommend it for lucidity and consequence. But without due attention to the variance of osmotic systems it is a difficult and an arbitrary matter to introduce the important phenomena, which they present, into a satisfactory treatment of thermodynamic equilibria in particular or of physical chemistry in general.

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