It is probable that the slight discrepancy between the dichromate and the permanganate (or iodine) methods is due to an oxygen error of less than 0.1% in the dichromate-iodide reaction.

A theory is suggested for the catalysis of the reaction between oxygen, iodide and acid during the reduction of dichromate by iodide.

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THE APPLICATION OF THE PHASE RULE TO GALVANIC CELLS

BY JAMES A. BEATTIE[1]

The deduction of the phase rule by any of the many methods that have been used requires that the separate parts of the system under consideration be in equilibrium. It is therefore necessary, before proceeding to apply the phase rule to galvanic cells, to discuss them from this standpoint.

A system is in stable equilibrium when, if any of its internal variables (such as pressure, temperature, concentration, etc.) is slightly changed, the state of the system adjusts itself so as to oppose this change; and if this disturbing influence is removed, the system will restore itself to its original state. The case of neutral equilibrium, in which an infinitesimal disturbance of an internal variable causes no alteration in the state of the system, seldom if ever occurs in chemical systems and hence will not be considered here.

In general, galvanic cells, when their potentials are exactly balanced by an opposing electromotive force, as when measured on a potentiometer, may be considered to be in equilibrium.[2] Consider the concentration cell

$$\text{Pt, } H_2(1 \text{ atm.}) \mid \text{HCl } (C') \mid \text{HCl } (C'') \mid H_2(1 \text{ atm.}), \text{ Pt} \qquad (A)$$
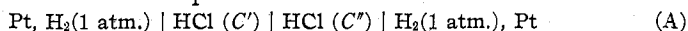
when its potential is so balanced. If the applied electromotive force is slightly increased (other conditions being kept constant) current will flow through the system in such a manner as to transfer HCl from the more dilute to the more concentrated solution, thus increasing the potential of the cell; and if the external electromotive force is restored to its original value, current will flow through the cell in the opposite direction until the concentrations of the solutions are again C' and C''. The other variables of the system can be treated in the same manner, and hence the system is in equilibrium.

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[2] Throughout this discussion the electromotive force of the cell is always considered as balanced by an equal and opposite potential. A cell that is in equilibrium under these conditions will also be in equilibrium when connected to a condenser (or, what amounts to the same thing, is on open circuit). Adding an electric charge to the plates of the condenser or subtracting one from them corresponds to increasing or decreasing the potential opposing that of the cell.

Certain cells, among which are those having electrolytes with only one ion in common, such as

$$\text{Ag} \mid \text{AgCl}, \text{NaCl} \ (C) \mid \text{KCl} \ (C), \text{AgCl} \mid \text{Ag} \qquad\qquad \text{(B)}$$
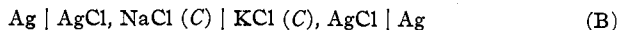
have been found to give variable potentials when the liquid junction is made in the ordinary way, and hence are not in equilibrium. These cells will be discussed later.

It may be well to consider here the effect of diffusion. It is evident that Gibbs[3] believed that cells in which diffusion takes place are not equilibrium systems and hence not capable of phase-rule treatment. This is without doubt true, if the problem under consideration is the final state at which the system arrives after a very long time. There would then be no electrical potentials whatever present. It is now generally recognized, however, that in many cases several different equilibria are being established within the same system and that the phase rule is applicable to each, provided cognizance of this time factor is taken. Such is the case of the equilibria between liquid and vapor acetic acid and between acetic acid and its elements. It will be shown that in every galvanic cell containing a liquid phase, diffusion takes place. Yet, in general, with respect to the time necessary to establish and measure the electromotive force of the cell, the "state of the system" from a phase-rule standpoint has not changed due to diffusion (that is, the potential of the cell has remained constant) and hence a phase-rule discussion of these systems is in order. Several interesting cases, of which Cell B above is an example, where diffusion produces a practically instantaneous effect on the state of the system will be discussed later.

In all of the following discussion, the electrodes will always be considered reversible to the solution, that is, there are no irreversible effects such as overvoltage or passivity. The usual ideas regarding reversible processes are employed, namely, when current is allowed to flow through the cell the applied electromotive force must exceed that of the cell by only an infinitesimal amount.

In the application of thermodynamics to galvanic cells, it is convenient for purposes of writing the necessary equations to consider that the boundary between two phases at which a potential occurs is very thin, that is, the junction is so sharp that it is not necessary to treat the boundary portion as an extra phase. In experimentally measuring the potential of simple concentration cells similar to that shown at A it is often desirable to make a liquid-liquid boundary quite wide, but it has been shown that the potentials measured in this way are the same as those obtained when the liquid junction is made very thin by a flowing method.[4] However,

[3] "Scientific Papers of J. Willard Gibbs," Longmans, Green and Co., 1906, vol. I, pp. 338, 429.

[4] MacInnes and Beattie, THIS JOURNAL, 42, 1117 (1920).

if it is desired to consider the boundary portion as one or more extra phases, it will be shown later that the phase rule automatically takes care of this case.

During the following theoretical discussion, the system will be treated as though diffusion does not take place at the boundary between two phases. The above assumptions define what Gibbs called a perfect electrochemical apparatus and, although no actual cell possesses all of these properties, we will have in mind the ideal case during the derivation of the phase rule, and study the effect of the deviations of actual cells from the ideal by an examination of several typical cases.

There are many methods of deducing the phase rule, but none, it appears to me, show so clearly the assumptions made and the relation between the variables as the derivation from the energy equation, which is the method used by Gibbs.[5]

Galvanic Cells in which All of the Phases are under the Same Pressure

Let ϵ be the energy of any homogeneous part or phase of a system of n components containing no electrical potentials. Then for any change, the differential of ϵ must satisfy the equation
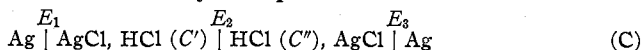
$$d\epsilon = T ds - p dv + \mu_1 dm_1 + \mu_2 dm_2 + \text{------} + \mu_n dm_n \qquad (1)$$

in which T and p are the temperature and pressure of the phase, ds and dv are the changes in total entropy and volume occurring, dm_i the change in mass of the i-th component, and μ_i its chemical potential. If the system consists of P phases, there is an equation similar to (1) for each phase.

If the passage of current through a system causes any of the components of a given phase to move through a boundary at which an electrical potential occurs there must be terms in the energy equation to take account of the fact that the total energy of the phase can be increased or decreased by the flow of electrical energy across this boundary. In galvanic cells a phase may contain one or two such boundaries; thus in Cell B each silver electrode contains one, and each liquid phase two. The electrical energy gained or lost by a phase at such a boundary is Edc and, since the potentials at the different junctions are in general different, there will be as many of these terms as there are surfaces containing potentials. Suppose that for a phase there are q such surfaces; Equation 1 then becomes

$$d\epsilon = T ds - p dv + \mu_1 dm_1 + \text{------} + \mu_n dm_n + E_1 dc_1 + \text{------} + E_q dc_q \qquad (2)$$

There is an equation similar to (2) for each phase containing an electrical potential at a surface through which any component moves upon the passage of current; and one similar to (1) for each phase at whose boundary such a process does not occur. It is evident that the same Edc term will occur in the equations for two adjacent phases. In the cell

$$\overset{E_1}{\text{Ag}} \mid \overset{}{\text{AgCl, HCl}} (C') \mid \overset{E_2}{\text{HCl}} (C''), \text{AgCl} \mid \overset{E_3}{\text{Ag}} \qquad (C)$$

[5] Ref. 3, p. 96.

the term E_1dc_1 will occur in the energy equations for both the silver phase and the first liquid phase, and E_2dc_2, in the equations for the two liquid phases. The solid silver chloride phase which is used to keep the hydrochloric acid solutions saturated[6] contains no surface at which electrical energy takes part and hence the energy equation for this phase will contain no electrical term.

Before proceeding further it is necessary to consider the meaning of the terms *component* and *phase.*

The number of components in a galvanic cell can be determined by the usual rule,[7] namely, that it is the least number of independently variable chemical constituents, by means of which it is possible to express all variations in the composition of every phase of the system under consideration.

The number of phases present is determined by the number of energy equations similar to (1) or (2) that it is necessary to write. The addition of the electrical term sometimes causes phases to be counted as distinct which would otherwise be counted as one. In the cell (C) above, the two silver electrodes would be counted as two separate phases, since the potentials at the surfaces of each are different and hence their energy equations would be different. But the two solid silver chloride phases are counted as one since there is no electrical term in the energy equation, and hence the ordinary rule, that a solid phase is counted only once, applies. Moreover, an inert metal electrode such as the platinum in Cell A is considered as only one phase since, although there is an electromotive force at its surface, the metal does not migrate with the passage of the current, that is, the conduction is electronic and not electrolytic.

Cells containing a single solution between two electrodes should be considered as having two liquid phases (one saturated with the material at one electrode, and the other saturated with respect to the other) separated by a surface containing a potential. Tolman and Ferguson[8] have measured the potential of the cell, Pt, H_2 (1 atm.) | HCl (C), HgCl | Hg, which according to the above principle should be written, Pt, H_2 (1 atm.) | HCl (C, sat. with H_2) | HCl (C, sat. with HgCl) | Hg. They found that when they stirred the solution by bubbling the hydrogen through it the electromotive force of the cell was very variable. This would corre-

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[6] In experimental procedure, the silver chloride is usually precipitated directly on the silver electrode, but theoretically the same result would be obtained by saturating the solution with AgCl, since its only function is to regulate the silver-ion concentration.

[7] It should be noted that the definition given by Washburn ["Principles of Physical Chemistry," McGraw-Hill Book Co., 1921, p. 388] (that the number of components is one greater than the number of percentage compositions which it is necessary to state to fix the composition of the most complex phase) will not in general give the correct number of components for galvanic cells. This is evidently due to the fact that in such systems even the most complex phase may not contain all of the components of the system.

[8] Tolman and Ferguson, THIS JOURNAL, 34, 232 (1912).

spond to measuring the potential of the first cell. Later measurements by Ellis[9] and by Linhart[10] in which anode and cathode portions were kept separate gave higher and much more concordant results. This is to be expected since if some of the dissolved hydrogen came into contact with the calomel electrode, or calomel with the hydrogen electrode, the reaction would take place on the electrode rather than in the cell as a whole,[11] and this would reduce the electromotive force. If the mixing were thorough the potential of the cell would probably drop to zero.

It will be shown that the application of the phase rule to cells of this type predicts that the first cell cannot be in equilibrium, and hence cannot give a constant potential, whereas the second is in equilibrium if its potential is properly balanced. In certain cells in which the essential reacting materials at the electrodes are so insoluble that practically no ions of these reacting materials, or at most only a few, exist in solution, mixing the anode and cathode portions of the electrolyte does not seem to affect the *measured* potential of the cell, but it is evident that for a thermodynamic discussion, these cells should be treated in the same manner as those containing more soluble substances at the electrodes.

Equation (2) contains as variables, the energy, temperature, entropy, pressure, volume, n masses, n chemical potentials, q electrical potentials, and q electrical charges, in all $2n + 2q + 5$. However, the partial differential equations, $\frac{\partial \epsilon}{\partial s} = T$ and $\frac{\partial \epsilon}{\partial v} = -p$, give two relations between ϵ,

s, T, p and v. Also the n equations, $\frac{\partial \epsilon}{\partial m_i} = \mu_i$, give n relations between ϵ,

the m's, and the μ's; and the q equations $\frac{\partial \epsilon}{\partial c_i} = E_i$, give q relations between ϵ, the c's and the E's. These equations together with the original Equation 2 give $n + q + 3$ relations among the variables.

The n masses can be split into $n - 1$ independent ratios of masses (or concentrations) and the total mass of the phase M. The n-th concentration is obtained by subtracting the sum of the $n-1$ others from unity. Since the total mass of a phase does not affect equilibrium, this further reduces by one the number of independent variables. Hence the $2n + 2q + 5$ variables of Equation 2 are subject to $n + q + 4$ restrictions leaving $n + q + 1$ of them independent; in Equation 1 there are $n + 1$ independent. Any set of $n + 1$ independent variables can be chosen to fix the state of the phase under consideration.

Consider now a galvanic cell of P phases, containing S surfaces at which

[9] Ellis, THIS JOURNAL, **38**, 737 (1916).

[10] Linhart, *ibid.*, **41**, 1175 (1919).

[11] In order to get an electromotive force from a reaction it is necessary to separate it into two portions, one of which evolves electrons and the other absorbs them.

electric potentials exist. In writing the equations for the energy of the
system we will assume that every phase contains some of each component,
and later show how the equations are affected when such is not the case.

$$\delta\epsilon' = T'\,\delta s' - p'\,\delta v' + \mu_1'\delta m_1' + \text{------} + \mu_n'\delta m_n' + E_a\delta c_a \qquad (3)$$
$$\delta\epsilon'' = T''\,\delta s'' - p''\delta v'' + \mu_1''\delta m_1'' + \text{------} + \mu_n''\delta m_n'' + E_a\delta c_a + E_b\delta c_b$$
$$\vdots \qquad \vdots \qquad \vdots \qquad \vdots$$
$$\delta\epsilon^P = T^P\delta s^P - p^P\delta v^P + \mu_1{}^P\delta m_1{}^P + \text{------} + \mu_n{}^P\delta m_n{}^P + E_S\delta c_S$$

The primes 1 to P refer to the number of the phases; the subscripts 1
to n, to the number of the components, and the subscripts a to S to the num-
ber of surfaces containing electrical potentials. Some phases may contain
only one such surface, some two, and some none, but for the derivation
of the phase rule it is necessary to consider only the number of such
surfaces, and not the way they are distributed among the phases.

Consider first the case in which there are no surfaces containing elec-
trical potentials, nor any osmotic membranes in the system. When such
a system is in equilibrium the variation of the total energy of the system
must be zero or positive for all variations which do not conflict with the
equations of condition of the system, which are that its entropy and volume
are constant, and that the total quantity of each constituent remains un-
changed. It has been shown[12] that in this case the necessary and suffi-
cient conditions for equilibrium are that the temperature, pressure and
chemical potential of each component be the same for every phase.

$$T' = T'' = \text{------} = T^P \qquad (4)$$
$$p' = p'' = \text{------} = p^P \qquad (5)$$
$$\mu_1' = \mu_1'' = \text{------} = \mu_1{}^P \qquad (6)$$
$$\vdots \qquad \vdots \qquad \vdots$$
$$\mu_n' = \mu_n'' = \text{------} = \mu_n{}^P$$

Each horizontal line represents $P-1$ equations, and there are $n + 2$
such lines; hence there are $(P-1)\,(n + 2)$ condition equations on the
variables of the system, due to the various phases being in equilibrium.

In the case of a galvanic cell in which all the phases are under the same
pressure, Equations 4 and 5 still hold, but not the set of Equations 6.
This is due to the existence of electrical energy at the surface of some of
the phases; also some phases do not contain all of the components of the
system. It can be shown, however, that there are still the same number
of equations between the chemical potentials as are given in 6.

In a galvanic cell, as shown at (C), there are three different types of
equations between the chemical potentials.

(a) If there is no surface containing electrical energy between two
phases, the chemical potentials of the components in the two phases are
equal. This is the case of the dissolved and solid silver chloride.

(b) If a component is not present in a given phase, the $\mu\delta m$ term for
that component will not appear in the energy equation for the phase under
consideration. There will be as many μ's lacking in Equation 6 as there

[12] Ref. 3, p. 65.

are components missing in the various phases.   If the substance is a possible (though perhaps not actual) component, then the value of the chemical potential is equal to or greater than some value M determined by the state of the system.[13]

(c) If a component takes part in the passage of electricity from one phase to another there is still a relation between the chemical potentials in the two phases.   Consider that the amount δm_1 of a component is transferred across a phase boundary by the passage, under equilibrium conditions, of a quantity δc of electricity: then if all other factors are held constant the electrical and chemical works must be equal[14] or $\mu_1'\delta m_1 - \mu_1''\delta m_1$ $= E\delta c$; $\mu_1' - \mu_1'' = E\dfrac{\delta c}{\delta m_1}$.   Now $\delta c/\delta m_1$ is the quantity of electricity necessary to transfer unit mass of the component, and is a constant for any given component; hence[15] $\mu_1' - \mu_1'' = KE$.

There is such an equation for every ion passing through a boundary containing an electrical potential.   If two components take part in the passage of electricity through such a surface, as in the liquid junction between two electrolytes, there is a similar equation for each component, the same electromotive force being used in each case, but the appropriate value of K substituted.

The above equation can be considered as a condition equation connecting the μ's for each ionic component, since the electrical potential E has already been counted as a variable.

By means of the above considerations it can be seen that whenever one of the restrictions on the chemical potentials in (6) does not hold, another relation has been substituted, so that there are in the case of the galvanic cell as many relations between the chemical potentials as given in (6), that is $(P-1)n$.   Hence, the total number of equations between the variables is $(P-1)(n+2)$.

Without counting the electrical potentials there are $n+1$ variables in each phase, or $P(n+1)$ in all and there are S potentials making a total of $P(n+1)+S$.   These are connected by the $(P-1)(n+2)$ equations; hence, the number of independent variables V is equal to $n+2-P+S$.

Now if any arbitrary restrictions are placed on the system such as the fixing of the pressure, temperature, etc., the number of independent variations V is further reduced by one for each of these arbitrary re-

[13] Ref. 3, p. 66.

[14] Ref. 3, p. 333.

[15] If the pressures on the two phases are not the same, as in the case considered in a later paragraph, there is a term in this equation and the two preceding ones, taking account of the volume work done.   There may be such a term even when the pressures on the two phases are the same, if the system is not subjected to the condition that its total volume must be constant.   However, the equation still represents a relation between the chemical potentials, and does not involve any variables not already counted.

strictions,[16] hence the complete algebraic statement of the phase rule becomes

$$V = n + 2 - P + S - R \tag{7}$$

When there are no electrical potentials in the system under consideration, Equation 7 reduces to the phase rule that is applied to ordinary systems.

For every surface containing an electrical potential, the variance increases by unity; or for each surface containing an electrical potential the number of phases in which the system can be distributed is increased by unity.

Application of the Phase Rule to Specific Systems in which All the Phases Are under the Same Pressure

Before proceeding to apply the phase rule to galvanic cells it may be well to summarize what is meant by the various terms in the equation $V = n + 2 - P + S - R$.

The variance V is the number of independent variables, that is, the number of variables it is necessary to specify to fix the state of the system.

The number of components n can be determined by the rule given above.

The number of phases P is the number of homogeneous parts of the system. Two electrodes of the same material at which there are different potentials are counted as two phases, in case the electrode material takes part in the passage of the current through the surface, and one phase when the electrode is inert. A single electrolyte containing two different electrodes must be divided into two phases separated by a surface containing an electrical potential, as in the first case given below.

The S is the number of surfaces at which electrical potentials occur, and R, the arbitrary restrictions imposed on the system, such as the fixing of the temperature, pressure, etc.

Case I. Pt, $H_2(p$ atm.) | HCl (C) | $Cl_2(p$ atm.), Pt.—If the phase rule is applied to the cell *as written*, the computed variance is greater than the one experimentally found. There are four components, platinum, water, hydrogen and chlorine, four phases, and two surfaces containing electrical potentials.

Hence, $V = 4 + 2 - 4 + 2 = 4$. There are four variables—pressure, temperature, concentration of hydrochloric acid, and the electromotive force of the cell, of which only three are independent. Yet the phase rule states that there are four independent variables. This discrepancy shows that the system under consideration is not in equilibrium, which was the conclusion drawn from the work of Tolman and Ferguson in which they measured the potential of a similar cell, keeping the liquid phase homogeneous by stirring.

Suppose the cell is rewritten with an anode and a cathode phase, both containing hydrochloric acid of concentration C, but one saturated with

[16] See Richards, THIS JOURNAL, **38**, 983 (1916).

hydrogen at p atmospheres, and the other with chlorine, there being an electrical potential at the liquid junction, Pt, H_2 (p atm.) | HCl (C, sat. with H_2) | HCl (C, sat. with Cl_2) | Cl_2 (p atm.), Pt. There are still four components, but there are now five phases, three surfaces containing electrical potentials, and one restriction, namely, that the concentration of hydrochloric acid in the two liquid phases should be the same, whatever value C may have. Therefore, $V = 4 + 2 - 5 + 3 - 1 = 3$; and, hence, if any three variables of the system are fixed, the state is entirely determined. The phase rule does not tell which of the variables are independent, but only the maximum number. Pressure, temperature, concentration of hydrochloric acid, the three junction electromotive forces E_1, E_2, E_3 and the total potential of the cell E are all variables of the system, and fixing any three independent variables determines all the others. Thus if E_1, E_2 and p, or T, p and E_3, or T, p and C are known, the state of the system is determined. In general, the latter case—the variation of the total potential of the cell with temperature, pressure and concentration of hydrochloric acid—is the one most often considered.

If the temperature and pressure are fixed, R becomes 3 and $V = 1$. The potential is then a function of the concentration alone.

Case II. Ag | AgCl, LiCl (C') | LiCl (C''), AgCl | Ag.—There are four components: silver, chlorine, lithium, and water. There are five phases: two liquid, solid AgCl, and two solid Ag, and three surfaces containing electrical potentials. Hence, $V = 4 + 2 - 5 + 3 = 4$, and the potential of the cell is determined by the pressure, temperature and two concentrations of lithium chloride.

If now a solution of lithium chloride of concentration intermediate between C' and C'' is inserted between the two electrolytes—as is done in measuring the potential of the cell—the variance is not changed, since an extra phase and an extra surface containing a potential have been added, one of which affects V negatively and one positively. Hence the phase rule indicates that the concentration of this intermediate solution (between limits, of course) is immaterial, which has been shown experimentally. We could also consider that an indefinite number of intermediate phases exists, each with an additional potential, $i.$ $e.$, that the concentration of the intermediate solution varies gradually from C' to C''.

Case III.—Consider the application of the phase rule to the cell, Ag | AgCl, KCl (C) | NaCl (C), AgCl | Ag, in which the molal concentration of the two solutions is the same. There are five components, five phases, three surfaces containing potentials, and the one restriction that the two concentrations of the electrolytes shall be the same.[17] Hence,

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[17] The phase rule does not indicate any particular mode of expressing concentration. Yet even on any basis (such as percentage by weight) there would be a restriction, namely, that the fraction of chloride-ion constituent in the two liquid phases shall have a certain ratio.

$V = 5 + 2 - 5 + 3 - 1 = 4$. The variables of the cell are the pressure, temperature, concentration C, and the electromotive force. It is natural to suppose that only three of these are independent, yet the phase rule gives a variance of four. This would indicate either that this cell is not in equilibrium, or that the various quantities appearing in the phase rule have not been correctly counted. In either case the phase rule predicts that there is something peculiar about this cell. Lamb and Larson[18] have studied cells of this type, in which the solutions have only one ion in common, and they found that the potentials were variable unless the liquid junction was made in a particular way, by means of a "flowing junction." That is, when the liquid junction is made by the ordinary static method (even if diffusion is reduced to a minimum by the use of a ground glass connection at the boundary), the system is not in equilibrium, since the potential of the cell varies with the time. The fact that the use of a flowing liquid junction[19] caused the potential to become constant shows that the irreversibility in the cell with a static junction is at the liquid junction itself.

This method of fixing the potential at a boundary by a particular process removes the cause of the system not being in equilibrium, and hence may be considered as a restriction placed on the cell so as to make it behave as if in equilibrium. In the phase-rule equation there are then two restrictions, whence $R = 2$, so V becomes 3, and the system is trivariant as would be expected.

In general when the calculated variance is greater than is expected, it indicates that the system, as written, is not in equilibrium, for the reason (a) that the system was not correctly divided into phases; or (b) that the system under consideration *cannot* be in equilibrium; or (c) that some additional restriction, or restrictions, must be imposed so as to remove an irreversibility from the system.

The particular method of determining what restriction is necessary to cause the system to be in equilibrium is, of course, a matter for experiment for each case. All that the phase rule predicts is that the cell will not be in equilibrium when the connections between phases are made in the usual manner.

18 Lamb and Larson, THIS JOURNAL, 42, 229 (1920).

19 The difference between a static and a dynamic liquid junction is evidently that in the former case, any concentration change due to diffusion that occurs, persists and becomes greater as time goes on, but in the latter case such changes are immediately destroyed by the production of a fresh boundary. In some cells, such as the ordinary concentration cell, diffusion does not affect the liquid junction potential, but in the cell under consideration it evidently does. In an earlier paragraph a distinction was made between an irreversibility which changes the state of the system from a phase rule standpoint and one which does not. An example of the former is diffusion in the cell considered in Case III, and of the latter diffusion in the cell of Case II.

Galvanic Cells in which the Phases Are under Different Pressures

To illustrate the application of the method given above for deducing the phase rule for any system, consider a cell in which all the phases are not under the same pressure. Suppose that in the system under consideration there are π different pressures.

It will not be necessary to rewrite the energy equations, but only to consider the change introduced in Equations 4, 5 and 6. Not counting the pressures or electrical potentials, there are n variables in each phase, and nP variables in the P phases. In addition, there are S electrical potentials, and π different pressures, or $Pn + S + \pi$ variables in the system. Equation 4 still holds, and there are also, as before, $(P-1)n$ equations conditioning the Pn chemical potentials, which gives $(P-1)(n+1)$ equations connecting the variables of the system. The variance then becomes

$$V = Pn + S + \pi - (P-1)(n+1) = n + 2 - P + S - R + (\pi-1) \quad (8)$$

This is the general equation for any galvanic cell of n components distributed in P phases, separated by S surfaces containing electrical potentials and under π entirely different pressures. Equation 7 is a special case, in which all the phases are under the same pressure, that is, $\pi = 1$.

As an example take the cell Pt, $H_2(p_1$ atm.) | HCl (C molal p_2 atm., sat. with H_2 at p_1 atm.) | HCl (C molal p_2 atm., sat. with H_2 at p_3 atm.) | H_2 (p_3 atm.), Pt. There are four components, five phases, three surfaces with potentials, three different pressures—p_1, p_2 and p_3—and the restriction that the hydrochloric acid concentration in the two liquid phases shall be the same. The variance is $V = 4 + 2 - 5 + 3 - 1 + (3-1) = 5$, and the system becomes nonvariant when the temperature, concentration of hydrochloric acid, and the three pressures are fixed.

General Derivation of the Phase Rule

The method given above of deriving the phase rule is applicable to any system in equilibrium, if the energy equation can be written for each phase. The general energy equation has the form

$$d\epsilon = Tds - pdv + \mu_1\,dm_1 + - + \mu_n dm_n + A_1 da_1 + A_2 da_2 + - \quad (9)$$

where A_1, A_2— are intensity factors and a_1, a_2— capacity factors of the various forms of energy (other than heat, volume and chemical energy) manifested in the phase.

There must be a term in Equation 9 for each way that energy can leave or enter the phase. Hence, to determine what variables it is necessary to consider as affecting the equilibrium, it is only necessary to find out those that affect the energy of the individual phases.

Thus in disperse phases, the extent of division of the phase will not affect the equilibrium unless the particles are small enough to require a term for the surface energy, $\gamma_1 dS_1$, in the energy equation, γ being the surface

tension and S the surface. If such a term is required, the equilibrium is affected by the state of division of the phase, and the phase rule derived for this system would be different from that ordinarily given. It is also evident that all the particles must be the same size so that γ is the same for each one; if several sizes of particles are allowed there must be a term in the energy equation for each size since γ would be different for each. It is easily seen that the phase rule derived for a system containing S different surface tensions would be the same as that for a system having S surfaces containing potentials, namely, $V = n + 2 - P + S - R$, S now representing the number of numerically different surface tensions in the system.

This equation was deduced in a somewhat different manner by Pavlov[20] and also by Tolman,[21] but it seems that the derivation from the energy equation is the most direct, and gives the best information as to what variables it is necessary to consider as affecting the equilibrium.

Summary

It has been shown how the phase rule can be deduced for any system in equilibrium.

The phase rule has been deduced for galvanic cells when in equilibrium, the variance being given by the expression, $V = n + 2 - P + S - R + (\pi - 1)$, where n is the number of components distributed in P phases, separated by S surfaces containing electrical potentials, and under π different pressures. R is the number of arbitrary restrictions imposed. In general all the phases are under the same pressure, and in this case, $V = n + 2 - P + S - R$.

When the variance calculated by this equation is greater than that expected, it indicates: (a) that the system was not correctly divided into phases or, (b) that the system under consideration cannot be in equilibrium or, (c) that some additional restriction, or restrictions, must be imposed so as to remove an irreversibility from the system.

The phase rule has been applied to several cells. The following points have been made.

(a) The number of phases is determined by the number of energy equations it is necessary to write. Thus two silver electrodes having different potentials at their surfaces must be considered separate phases, since their energy equations are different. The same applies to two colloidal phases of the same material but with different surface tensions.

(b) A cell containing two electrodes and one solution must be considered as having two liquid phases (one saturated with the material at one electrode, and the other saturated with respect to the other) separated by a

[20] Pavlov, Z. physik. Chem., **75**, 48 (1910).

[21] Tolman, This Journal, **35**, 307, 317 (1913).

surface containing a potential; and the cell is not in equilibrium and hence will not give a constant electromotive force, if the two portions are mixed.

(c) Cells containing a liquid junction between two solutions having a single ion in common are not in equilibrium unless there is a restriction placed on the method of making the liquid junction, so as to remove an irreversibility at this boundary.

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NOTES

An Attempt to Measure the Potential of the Fluorine Electrode.— Elementary fluorine is apparently the strongest oxidizing agent that has yet been prepared, as is seen from its extreme chemical activity and the ease with which it replaces oxygen and chlorine from their compounds. A determination of the potential of the fluorine electrode would therefore be of very great interest, and serve as a basis for the calculation of the free energies of fluorine compounds.

The only attack upon this problem of which we are aware is the rough estimate of the free energy of formation of hydrogen fluoride gas made by Lewis and Randall[1] using an empirical rule suggested by Eastman. The problem, although obviously difficult from an experimental standpoint, was so inviting in view of its importance that we attempted to measure the electromotive force of a cell consisting of a hydrogen electrode and a fluorine electrode with an electrolyte containing both hydrogen and fluoride ions and in which the activity of hydrogen fluoride either is known or may be determined. Two such liquids are fused potassium acid fluoride and liquid anhydrous hydrofluoric acid containing some ionized material such as potassium fluoride. Aqueous or organic solvents may not be used due to the violence of the reaction of fluorine with water and organic materials.

Although we were unsuccessful, a brief account of the experiments may be of value in guiding others who later attempt the same task.

Anhydrous hydrofluoric acid failed to work for two reasons. The first and most important of these is that no electrode material could be found that would withstand the combined action of fluorine and hydrofluoric acid. Platinum, iridium, gold, and nickel all react with fluorine under these conditions. Moissan[2] was able to obtain only a 20% yield of fluorine from a platinum electrode in hydrofluoric acid at low temperatures, the rest of the fluorine going to form platinum fluoride. After trying these metals there remained only one material, graphite, which

[1] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., **1923**, p. 463.

[2] Moissan, *Compt. rend.*, **102**, 1543 (1886); **103**, 202, 256 (1886).