

EXTENDED FORM OF THE GIBBS PHASE RULE

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THE FOLLOWING EXTENDED form of the Gibbs Phase rule can be used to determine the degrees of freedom possessed by a system consisting of several species which partake in one or more chemical reactions.

$$f = (N - r - s) - p + 2 - t + u \quad (1)$$

where f = degrees of freedom

N = species

r = independent reaction equilibria

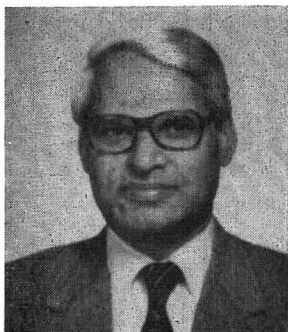
s = stoichiometric constraints

p = phases

t = special or additional constraints

u = special or additional variables

A species is defined as a chemically distinct entity. For instance, in a system comprised of $H_2O(g)$ and $H_2O(l)$ the number of species is but one. On the other hand, in the $H_2(g) - O_2(g) - H_2O(g)$ system, there are three species. In any system, once the species that occur have been



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identified then the corresponding atom matrix can be constructed. For this purpose, each species is represented by a line vector of atom coefficients. For the said $H_2(g) - O_2(g) - H_2O(g)$ system we obtain

| | H | O |
|-----------|---|---|
| $H_2O(g)$ | 2 | 1 |
| $H_2(g)$ | 2 | 0 |
| $O_2(g)$ | 0 | 2 |

The resulting atom matrix is reduced to an echelon form utilizing standard procedures [1]. This gives

$$\begin{bmatrix} 2 & 1 \\ 2 & 0 \\ 0 & 2 \end{bmatrix} \rightarrow \begin{bmatrix} 1 & \frac{1}{2} \\ 0 & 1 \\ 0 & 0 \end{bmatrix} = E$$

The rank of the echelon matrix E , defined as the number of non-zero rows, is seen to be 2. This also happens to be the rank of the parent matrix. Thus

$$c^* = \text{rank of the atom matrix} = 2.$$

It is well to note that underlying this system, there are but two kinds of atoms—namely H and O. Thus, the above findings with regard to the rank of the atom matrix may appear to be entirely predictable; and it may be supposed that c^* is equal to k where k is defined as the kinds of atoms that comprise the species present in the system. However, careful examination uncovers the fallacy of such a supposition. The following example illustrates the point. In the $CaCO_3(s) - CaO(s) - CO_2(g)$ system, it is clear that there are three kinds (Ca, C, and O) of atoms. The corresponding atom matrix is constructed as follows:

| | Ca | C | O |
|-------------|----|---|---|
| $CaCO_3(s)$ | 1 | 1 | 3 |
| $CaO(s)$ | 1 | 0 | 1 |
| $CO_2(g)$ | 0 | 1 | 2 |

This is reduced to the echelon form in the usual

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manner.

$$\begin{bmatrix} 1 & 1 & 3 \\ 1 & 0 & 1 \\ 0 & 1 & 2 \end{bmatrix} \rightarrow \begin{bmatrix} 1 & 1 & 3 \\ 0 & 1 & 2 \\ 0 & 0 & 0 \end{bmatrix} = E$$

Thus, the rank c^* of the atom matrix is only 2 despite the fact that there are three kinds of atoms underlying the species. In general,

$$c^* \leq k \quad (2)$$

The number of independent reactions that occur in a system comprised of N species is linked to the rank of the atom matrix in accordance with the Gibbs stoichiometric rule [2].

$$0 < r \leq (N - c^*) \quad (3)$$

The equality sign gives r^* the maximum number of linearly independent reactions that are required to describe the system. Therefore, f^* , the minimum number of degrees of freedom the system possesses becomes equal to

$$f^* = (* - s) - p + 2 - t + u \quad (4)$$

where $c^* = (N - r^*)$, and r^* is the maximum number of linearly independent reactions occurring in the system.

NUMBER OF COMPONENTS AND STOICHIOMETRIC CONSTRAINTS

The number of components (c) of a system is the smallest number of chemical species (or constituents) that must be specified in order to completely define the composition of the phases involved in the equilibrium. For a phase composed of α constituents, in the absence of stoichiometric constraints, one must specify $(\alpha - 1)$ mole fractions in order to fully define its composition. The last remaining mole fraction can be obtained, by difference, from the equation

$$x_1 + x_2 + \dots + x_{\alpha-2} + x_{\alpha-1} + x_\alpha = 1.0 \quad (5)$$

The number of components is not necessarily the same as the number of elements, or chemical species, or compounds present in the system.

The number of components can be greater than, equal to, or less than the number of initial substances from which the equilibrium system is synthesized in the laboratory. The number of com-

ponents, c , is not necessarily equal to the rank of the atom matrix constructed with the species occurring in the system under consideration. In general

$$c \leq c^* \leq k \quad (6)$$

where c^* and k have the same meaning as before. It will be noted that in the absence of any stoichiometric constraints, $c = c^* = (N - r^*)$.

It is important that we have a clear understanding of the concept of stoichiometric constraint. The *stoichiometric constraint* is a unique constricting relationship between the mole fractions of two or more species occurring in a given phase. It is well to note that the scope of the stoichiometric constraint does not extend beyond the particular phase that is under consideration. The constraint can be formulated in terms of mole fractions, as mentioned earlier, or in terms of partial pressures; and sometimes it is also expressed in terms of numbers of moles of species. Despite the fact that the numbers of moles of species are extensive variables (whereas the phase rule is a relationship between intensive variables), there is no internal inconsistency in this approach because the moles of species occurring in a given phase can be readily converted into mole fractions by division with total moles in that phase.

There is a distinction to be made between the stoichiometric constraint (in the present sense of the word) and the material balance equation; this distinction is most apparent in heterogeneous systems. A relationship that links numbers of moles of species from two or more phases ceases to be a stoichiometric constraint and simply becomes a material balance equation. This does not, however, preclude the reduction of two or more material balance equations into one or more stoichiometric constraints by appropriate algebraic operations. Also, one cannot write a stoichiometric constraint for a given phase that is in violation of the material balance equation for the larger system.

The number of components (c) in the system is given by

$$c = c^* - s = (N - r^* - s) \quad (7)$$

where s is the number of stoichiometric con-

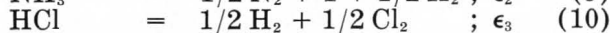
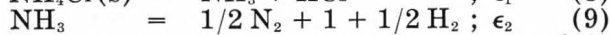
straints totaled over all the phases present in the system.

The existence of the stoichiometric constraint can be demonstrated quite rigorously by the use of the concept of "extent of reaction." A stoichiometric constraint is said to exist (i) if the atom ratio in a particular phase is equal to a ratio of two small integers, or (ii) when a simple relationship can be written linking two or more atom ratios in a particular phase. The following examples are instructive.

Suppose a system is prepared by placing an arbitrary amount of $\text{NH}_4\text{Cl}(\text{s})$ in an evacuated vessel. The temperature is raised, causing a portion of the salt to decompose into gaseous

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products. The species present in the system include $\text{NH}_4\text{Cl}(\text{s})$, NH_3 , HCl , N_2 , H_2 , and Cl_2 . Since the rank of the atom matrix is 3, it follows that there are three linearly independent reactions. These reactions and the corresponding extents of reaction are



The number of moles of each species can be written in terms of the initial values and the extents of reaction.

$$n(\text{NH}_4\text{Cl}) = n^\circ(\text{NH}_4\text{Cl}) - \epsilon_1$$

$$n(\text{NH}_3) = \epsilon_1 - \epsilon_2$$

$$n(\text{HCl}) = \epsilon_1 - \epsilon_3$$

$$n(\text{N}_2) = 0.5 \epsilon_2$$

$$n(\text{H}_2) = 1.5 \epsilon_2 + 0.5 \epsilon_3$$

$$n(\text{Cl}_2) = 0.5 \epsilon_3$$

There are five "new" species, all occurring in the gas-phase. The numbers of moles (or mole fractions) of these five new species are seen to be expressed in terms of three extents of reaction. This means that only three of these quantities are independent. This can be demonstrated quite readily by the matrix methods.

$$\begin{array}{c} \text{NH}_3 \\ \text{HCl} \\ \text{N}_2 \\ \text{H}_2 \\ \text{Cl}_2 \end{array} \begin{array}{ccc} \epsilon_1 & \epsilon_2 & \epsilon_3 \\ 1 & -1 & 0 \\ 1 & 0 & -1 \\ 0 & 0.5 & 0 \\ 0 & 1.5 & 0.5 \\ 0 & 0 & 0.5 \end{array} \rightarrow \begin{array}{ccc} \boxed{1} & \boxed{-1} & \boxed{0} \\ \boxed{0} & \boxed{1} & \boxed{-1} \\ \boxed{0} & \boxed{0} & \boxed{1} \\ \boxed{0} & \boxed{0} & \boxed{0} \\ \boxed{0} & \boxed{0} & \boxed{0} \end{array} = E$$

The echelon matrix (E) shown on the right has a rank of 3 indicating that only three independent vectors exist. Thus, intuitively, we anticipate the existence of two stoichiometric constraints. For the g.atoms of each element in the gas-phase, we have

$$\begin{array}{l} \text{N} = n(\text{NH}_3) + 2n(\text{N}_2) = \epsilon_1 \\ \text{H} = 3n(\text{NH}_3) + n(\text{HCl}) + 2n(\text{H}_2) = 4\epsilon_1 \\ \text{Cl} = n(\text{HCl}) + 2n(\text{Cl}_2) = \epsilon_1 \end{array}$$

Two independent atom ratios can be written between these three elements. Thus

$$\frac{\text{H}}{\text{N}} = \frac{4\epsilon_1}{\epsilon_1} = \frac{4}{1} ; \quad \frac{\text{H}}{\text{Cl}} = \frac{4\epsilon_1}{\epsilon_1} = \frac{4}{1}$$

Substitutions provide

$$n(\text{HCl}) + 2n(\text{H}_2) = n(\text{NH}_3) + 8n(\text{N}_2)$$

$$3n(\text{NH}_3) + 2n(\text{H}_2) = 3n(\text{HCl}) + 8n(\text{Cl}_2)$$

Division by the total number of moles of gaseous species yields

$$x(\text{HCl}) + 2x(\text{H}_2) = x(\text{NH}_3) + 8x(\text{N}_2) \quad (11)$$

$$3x(\text{NH}_3) + 2x(\text{H}_2) = 3x(\text{HCl}) + 8x(\text{Cl}_2) \quad (12)$$

where $x(i)$ is the mole fraction of the i th species in the gas-phase. Thus, we have uncovered two stoichiometric constraints (applicable in the gas-phase) for this system. That the atom ratios H/N and H/Cl in the product-gas mixture will be equal to 4/1 can be readily surmised by an inspection of the stoichiometry of the original $\text{NH}_4\text{Cl}(\text{s})$ species from which the gas-phase has evolved.

We can determine the number of components in this system by the application of Eq. (7). It will be noted that

$$\begin{array}{l} \text{N} = 6 \text{ (one solid + five gases)} ; r^* = 3 ; c^* = 3 \\ s = \text{Number of stoichiometric constraints} = 2 \end{array}$$

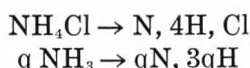
Substitutions yield

$$c = (6 - 3 - 2) = 1$$

We may now consider a variation of the foregoing illustration. Suppose that the system is prepared by placing a mixture of arbitrary amounts of $\text{NH}_4\text{Cl}(\text{s})/\text{NH}_3(\text{g})$ in an evacuated vessel and at equilibrium there are present HCl , N_2 , H_2 , and Cl_2 in addition to the two initial substances. It is readily seen that in this particular example, the atom ratios H/N and H/Cl of the gas-phase are not equal to 4/1. However, there does exist a simple

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relationship between the atom ratios. Since the initial mixture is composed of arbitrary amounts of the two constituents, let us suppose that it consisted of q moles of NH_3 per mole of $\text{NH}_4\text{Cl}(\text{s})$. Since the four new species are generated from these two compounds, we can write



Furthermore

$$\frac{\text{N}}{\text{Cl}} = \text{RNL} = 1 + q \quad ; \quad \frac{\text{H}}{\text{Cl}} = \text{RHL} = 4 + 3q$$

where RNL and RHL are atom ratios in the gas-phase. By eliminating q , we obtain the following relation that links the two atom ratios:

$$\text{RHL} = 3 \text{RNL} + 1 \quad (13)$$

In light of this, we can conclude that there indeed exists a stoichiometric constraint in this system. The same conclusion can also be reached in a slightly different way. In terms of extents of reaction

$$\begin{aligned}n(\text{NH}_4\text{Cl}) &= n^\circ(\text{NH}_4\text{Cl}) - \epsilon_1 \\ n(\text{NH}_3) &= n^\circ(\text{NH}_3) + \epsilon_1 - \epsilon_2 \\ n(\text{HCl}) &= \epsilon_1 - \epsilon_3 \\ n(\text{N}_2) &= 0.5 \epsilon_2 \\ n(\text{H}_2) &= 1.5 \epsilon_2 + 0.5 \epsilon_3 \\ n(\text{Cl}_2) &= 0.5 \epsilon_3\end{aligned}$$

Since the last four equations involve only three independent parameters, viz., ϵ_1 , ϵ_2 , and ϵ_3 , it is clear that only three of these equations are truly independent. The remaining can be obtained by a linear combination of the others. It is a relatively simple exercise to show that

$$3 n(\text{N}_2) = 1.5 \epsilon_2 = n(\text{H}_2) - n(\text{Cl}_2)$$

or

$$3 x(\text{N}_2) + x(\text{Cl}_2) = x(\text{H}_2) \quad (14)$$

which is the stoichiometric constraint for the system. The very same relationship can also be deduced by starting with Eq. (13).

In this system also we have $N = 6$, $c^* = 3$, and $r^* = 3$. Furthermore, $s = 1$. This provides

$$c = \text{Number of components} = c^* - s = 2$$

The systems $\text{NH}_4\text{Cl}(\text{s})/\text{HCl}(\text{g})$, $\text{NH}_4\text{Cl}(\text{s})/\text{N}_2(\text{g})$, $\text{NH}_4\text{Cl}(\text{s})/\text{H}_2(\text{g})$, and $\text{NH}_4\text{Cl}(\text{s})/\text{Cl}_2(\text{g})$

can be treated in a similar manner. In each of these, one can write a simple relationship with the atom ratios from which the stoichiometric constraint can be derived.

Let us consider a system that is prepared by placing $\text{MgSO}_4(\text{s})$ in an evacuated vessel and is allowed to equilibrate. The species present include $\text{MgO}(\text{s})$, SO_3 , SO_2 , SO , O_2 , S , S_2 , S_3 , S_4 , S_5 , S_6 , S_7 , and S_8 in addition to the original $\text{MgSO}_4(\text{s})$. The atom matrix has a rank of 3 and the maximum number of independent reaction equilibria is 11. The concentrations of the 12 new gaseous species generated in the system can be expressed in terms of 11 independent extents of reaction. Thus, there exists one stoichiometric constraint in the gas-phase. It can be easily shown that

$$\frac{\text{O}}{\text{S}} = \frac{3}{1} = \frac{3n(\text{SO}_3) + 2n(\text{SO}_2) + n(\text{SO}) + 2n(\text{O}_2)}{n(\text{SO}_3) + n(\text{SO}_2) + n(\text{SO}) + \sum_j n(\text{S}_j)} \quad (15)$$

This translates into the following stoichiometric constraint

$$x(\text{SO}_2) + 2 x(\text{SO}) + 3 \sum_j j x(\text{S}_j) = 2x(\text{O}_2) \quad (16)$$

Additionally $N = 14$, $c^* = 3$, $r^* = 11$ and $s = 1$. Substitutions yield

$$c = c^* - s = 2$$

This result is correct despite the fact that the system was prepared from a single substance.

While the method of extent of reaction is satisfactory for the purposes of formulating the stoichiometric constraints in a system, a simpler procedure may be advantageous in some instances. Suppose that a homogeneous system is prepared from I number of constituents. At equilibrium, this single-phase system contains N species of which I are the initial constituents. The rank of the atom matrix of N species is c^* and a maximum of r^* reactions are required to describe the system. We have

$$J = N - I \quad (17)$$

where J is the number of "new" species generated by the r^* reactions. The number of stoichiometric constraints s present in the system is given by

$$s = J - r^* = N - I - r^* = c^* - I \quad (18)$$

This relationship is directly applicable to single-

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GIBBS PHASE RULE

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phase systems only. For the more complex systems involving several phases, the more detailed 'extent of reaction method' should be employed.

The number of stoichiometric constraints in any particular phase is equal to the number of new chemical species (as distinguished from the 'old' or 'initial' species from which the system is prepared) occurring in that phase less the maximum number of linearly independent reactions required to describe the system. The number of components is equal to the rank of the atom matrix less the total number of stoichiometric constraints summed over all phases.

SPECIAL CONSTRAINTS

In contrast to the stoichiometric constraints which are preordained by the particular stoichiometry of the reaction system, the special constraint 't' has something of an arbitrary quality. One particular form this constraint often takes is that of specifying the pressure. For example, the total pressure of the system may be specifically fixed as in the case of equilibrium phase diagrams for alloy systems which are determined at a constant pressure of 1 atm. Alternatively, the partial pressure of a gaseous species (or the activity of a component in a condensed phase) may be specifically set at a particular value. Each such specific choice constitutes a special (or additional) constraint and results in a parallel loss in the degrees of freedom enjoyed by the system under consideration.

There is one kind of special constraint that resembles a stoichiometric constraint. This emanates from the condition of electroneutrality in ionic systems: the total charges on cationic species must exactly match those on the anionic species. In some systems, the electroneutrality constraint can be redundant because it may simply be a linear combination of independent stoichiometric constraints. So a check must always be made on the linear independence of the constraints before they are imposed on the system.

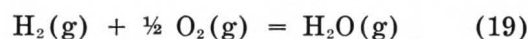
The effect of the special constraint on the number of components in a system is of some interest. When the imposed special constraint relates to phase-composition (i.e., mole fraction, partial pressure, or activity) it reduces the number of components in the same manner as does a stoichiometric constraint.

The discussion of the extended form of the Gibbs phase rule will not be complete without a consideration of its application. Each of the following examples is designed to illustrate a specific feature of the extended rule.

APPLICATIONS

H₂(g)-O₂(g)-H₂O(g) system

This is prepared by filling the vessel with a mixture of hydrogen, oxygen and water vapor. The system is allowed to equilibrate. It is seen that $N = 3$ and $c^* = 2$; hence $r^* = 1$. The lone independent reaction equilibrium is



There are no stoichiometric or special constraints; and no special variables are involved. Furthermore this is a single-phase system. Substitutions give

$$f = (3 - 1 - 0) - 1 + 2 - 0 - 0 = 3 \\ c = 2 - 0 = 2$$

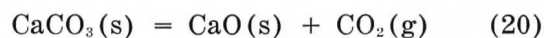
We can specify (1) temperature (2) total pressure and (3) a composition parameter such as the H/O atom ratio of the gas-phase.

$$\frac{\text{H}}{\text{O}} = \frac{2n(\text{H}_2) + 2n(\text{H}_2\text{O})}{n(\text{H}_2\text{O}) + 2n(\text{O}_2)} \\ = \frac{2P(\text{H}_2) + 2P(\text{H}_2\text{O})}{P(\text{H}_2\text{O}) + 2P(\text{O}_2)}$$

where $n(i)$ and $P(i)$ respectively denote the number of moles and partial pressure of the i th species.

CaCO₃(s)-CaO(s)-CO₂(g) system

Suppose that solid calcium carbonate is placed in an evacuated vessel and is allowed to dissociate and reach equilibrium. The species present in the equilibrated system are CaCO₃(s), CaO(s) and CO₂(g). As noted earlier, the atom matrix constructed of these three species has a rank of 2. The only reaction equilibrium to be considered is



No stoichiometric constraint exists because the products CaO(s) and CO₂(g) occur in different phases (unlike SO₂ and O₂ in the dissociation of solid MgSO₄ mentioned earlier). Thus $N = 3$, $c^* =$

2, $r^* = 1$, $p = 3$ and $s = t = u = 0$. Substitutions give

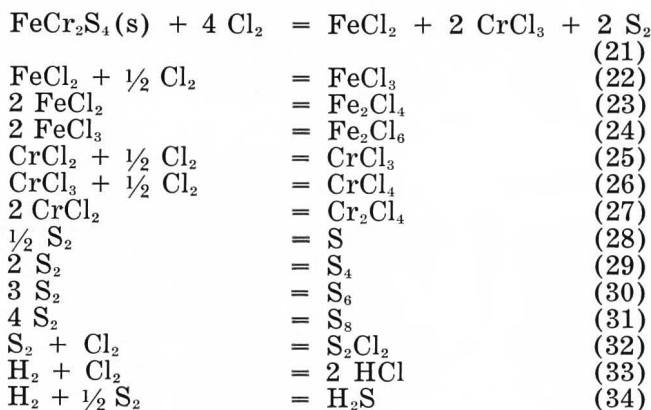
$$f = (3 - 1 - 0) - 3 + 2 - 0 = 1$$

$$c = 2 - 0 = 2$$

This is a univariant system which is completely described if temperature or pressure is specified.

FeCr₂S₄(s)-HCl(g)-Cl₂(g) system

This chemical transport system is prepared by placing a mixture of these three species in an evacuated vessel held at an appropriate temperature. At equilibrium the gas-phase is observed to contain 18 species: FeCl₂, Fe₂Cl₄, FeCl₃, Fe₂Cl₆, CrCl₂, CrCl₃, CrCl₄, Cr₂Cl₄, S, S₂, S₄, S₆, S₈, S₂Cl₂, H₂, Cl₂, HCl, and H₂S respectively, and no condensed phases other than FeCr₂S₄(s) occur. The atom matrix constructed of these nineteen species has a rank of 5. Thus $N = 19$ and $c^* = 5$; therefore $r^* = 14$. The maximum number of linearly independent reactions that are required to describe the system fully, thus, is seen to be 14. These are as follows



It is of particular interest to note that there are two stoichiometric constraints inherent in this manner of preparation of the vapor transport system. All of the Fe, Cr and S atoms in the gas-phase (albeit present in the form of various molecular species) originate with the solid FeCr₂S₄; also since no other condensed phase appears, the following obtains

$$\frac{\text{Cr}}{\text{Fe}} = \frac{2}{1} = \frac{P(\text{CrCl}_2) + P(\text{CrCl}_3) + P(\text{CrCl}_4) + 2P(\text{Cr}_2\text{Cl}_4)}{P(\text{FeCl}_2) + P(\text{FeCl}_3) + 2P(\text{Fe}_2\text{Cl}_4) + 2P(\text{Fe}_2\text{Cl}_6)}$$

$$\frac{\text{Cr}}{\text{S}} = \frac{2}{4} = \frac{P(\text{CrCl}_2) + P(\text{CrCl}_3) + P(\text{CrCl}_4) + 2P(\text{Cr}_2\text{Cl}_4)}{P(\text{S}) + 2P(\text{S}_2) + 4P(\text{S}_4) + 6P(\text{S}_6) + 8P(\text{S}_8) + 2P(\text{S}_2\text{Cl}_2) + P(\text{H}_2\text{S})}$$

Each of these relationships constitutes a stoichiometric constraint. There are no special constraints or variables that have to be reckoned with. Thus, we have

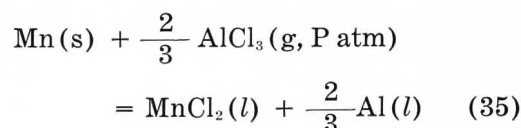
$$f = (19 - 14 - 2) - 2 + 2 - 0 = 3$$

$$c = 5 - 2 = 3$$

Three system properties have to be specified. These may be selected as (i) temperature (ii) initial chlorine pressure in the system, $P^\circ(\text{Cl}_2)$ and (iii) Cl/H atom ratio of the gas-phase. The specification of temperature yields 14 equilibrium constant expressions, one for each of the reactions identified above. These 14 relations together with the two stoichiometric constraint equations coupled with the values of $P^\circ(\text{Cl}_2)$ and Cl/H should enable the determination of the equilibrium partial pressures of the 18 gaseous species that occur in the system. An iterative method of calculation suitable for complex systems is presented in a recent publication [3].

Mn(s)-AlCl₃(g)-MnCl₂(l)-Al(l) system

For this four-phase, four species system, the atom matrix has a rank of three. The only independent reaction equilibrium is



Suppose that the pressure of AlCl₃(g) is arbitrarily set at 1 atm. This would constitute a special constraint. There are no stoichiometric constraints or special variables. Therefore $N = 4$; $r^* = 1$; $s = 0$; $p = 4$; $t = 1$ and $u = 0$. Substitutions yield

$$f = 0$$

$$c = c^* - s = 3$$

The system, when subject to the single special constraint stipulated above, becomes invariant. This simply means that there is but one unique temperature (T_e) at which the four-phase system is in a state of equilibrium for a $P(\text{AlCl}_3)$ of 1

atm. The value of T_e can be found as follows. For the reaction equilibrium

$$\Delta G = 0 = \Delta G_r^\circ(\text{MnCl}_2) - \left(\frac{2}{3}\right) \Delta G_r^\circ(\text{AlCl}_3)$$

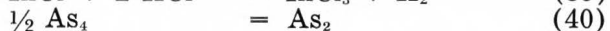
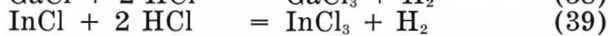
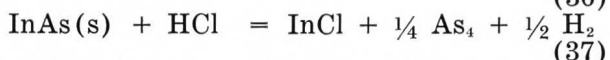
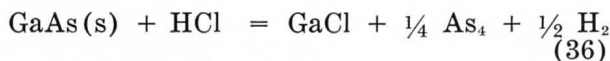
Using the tabulated data [4] on the standard free energies of formation (ΔG_r°), we find

$$\begin{aligned} 0 &= -39,162 + 41.601 T_e \\ T_e &= 941.4 \text{ K} \end{aligned}$$

The equilibrium $\text{Mn}(s) - \text{AlCl}_3(g) - \text{MnCl}_2(l) - \text{Al}(l)$ is unique in that it occurs only at this temperature when all the species are in their respective natural standard states. Had $P(\text{AlCl}_3)$ been specified as, say, 0.95 atm instead of 1.0 atm, then we would find that the corresponding value of T_e becomes 935 K. Only one special constraint may be imposed when $T_e = 935\text{K}$: for example, we cannot arbitrarily set $P(\text{AlCl}_3)$ at, say, 0.95 atm and at the same time fix the activity of aluminum (presumably present as a liquid alloy) at, say, 0.8. This would result in negative degrees of freedom which has no physical significance.

Ga-In-As-H-Cl system

The mixed crystal (solid solution) $\text{Ga}_x\text{In}_{1-x}\text{As}$ is grown from vapor phase. The system is prepared by introducing a gas mixture consisting of $\text{GaCl}(g)$, $\text{InCl}(g)$, $\text{As}_4(g)$, $\text{HCl}(g)$ and $\text{H}_2(g)$ into the crystal growth system. At equilibrium, there are present eight gaseous species (GaCl_3 , InCl_3 and As_2 in addition to the initial five) and two condensed phase species $\text{GaAs}(s)$ and $\text{InAs}(s)$. Since $c^* = 5$, it follows that $r^* = 5$. These five independent equilibria are:



There are no stoichiometric or special constraints. In order to facilitate the equilibrium calculation, however, sometimes two hypothetical species, $\text{GaAs}(g)$ and $\text{InAs}(g)$, are introduced. The number of moles of $\text{GaAs}(g)$ and $\text{InAs}(g)$ (hypothetically) present in the equilibrated system is simply equal to the number of moles of deposited GaAs and InAs respectively. The hypothetical

species constitute special variables. Thus $N = 10$; $r^* = 5$; $p = 2$; $s = t = 0$; and $u = 2$. Substitution gives

$$\begin{aligned} f &= (10 - 5 - 0) - 2 + 2 - 0 + 2 = 7 \\ c &= 5 - 0 = 5 \end{aligned}$$

These seven degrees of freedom are satisfied by specifying (1) temperature, (2) total pressure, (3) Cl/H atom ratio, (4) $n^\circ(\text{Ga})$, (5) $n^\circ(\text{In})$, (6) $n^\circ(\text{As})$, and (7) interaction parameter Ω for the GaAs-InAs regular solution. In here $n^\circ(\text{Ga})$, etc., denotes the number of g atoms of Ga, etc. in the initial gas-phase albeit present in the form of GaCl , etc. The atom balance equation for Ga is

$$n^\circ(\text{Ga}) = n^\circ(\text{GaCl}) = n(\text{GaCl}) + n(\text{GaCl}_3) + n^*(\text{GaAs})$$

where $n^*(\text{GaAs})$ represents the contribution due to the hypothetical species. Other atom balance equations can be written similarly.

FINAL COMMENTS

In attempting to make an equilibrium calculation in complex systems, a necessary and useful prerequisite is to conduct phase rule analysis of the system. Such an analysis helps clarify the essential elements of the calculation procedure. The extended form of the Gibbs phase rule presented here is especially useful in analyzing multicomponent heterogeneous systems. \square

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NOMENCLATURE

| | |
|-----------------------------------|---|
| c | number of components |
| c^* | rank of atom matrix |
| f | degrees of freedom |
| f^* | minimum number of degrees of freedom |
| $\Delta G_r^\circ(\text{AlCl}_3)$ | standard free energy of formation of $\text{AlCl}_3(g)$ |
| $\Delta G_r^\circ(\text{MnCl}_2)$ | standard free energy of formation of $\text{MnCl}_2(l)$ |
| I | initial constituents |
| J | new species |

| | |
|----------------------|---|
| k | kinds of atoms or elements |
| n(i) | number of moles of the ith species |
| n°(i) | initial number of moles of the ith species |
| N | species |
| p | number of phases |
| r | independent reaction equilibria |
| r* | maximum number of independent reaction equilibria |
| RHL | H/Cl atom ratio |
| RNL | N/Cl atom ratio |
| s | stoichiometric constraints |
| t | special or additional constraints |
| u | special or additional variables |
| x(i) | mole fraction of the ith species |
| Greek letters | |
| ϵ_i | extent of reaction for the ith reaction |

REVIEW: Diffusion in Liquids

Continued from page 29.

correlation of experimental data, via kinetic theory and, more extensively, such approximations as hydrodynamic and free volume theories. A separate section is provided for electrolytes. The utility of these theories is discussed for binary and ternary nonelectrolytes in Chapter 7 and for binary electrolytes and fused salts in Chapter 8.

This is a densely written book of high technical quality, and it is difficult to write a definitive review without extensive study, a procedure not feasible for this reviewer. However, I think it fair to say that this is a useful and reliable treatise, but that it will not attract large numbers of chemical engineers as readers. Much of the material presented is available elsewhere in equivalent form, and little attention has been paid to the problems of those wishing to use the subject matter in typical engineering applications. However, this book should prove valuable to those engaged in serious experimental or theoretical investigations and who wish to be sure that the basis of their work is sound. A few examples are given below to back up these comments.

The phenomenological discussion of Chapters 2 and 3 is representative of both the strengths and weaknesses of this book. The discussion of the Onsager reciprocal relation clears up a number of widely held misconceptions in a clear definitive manner, but little is done to provide the reader with convenient sets of diffusion equations, or of means to test and interrelate the wide variety of apparently different expressions found in the diffusion literature. The authors confine them-

selves largely to the flux expressions used by a relatively narrow group of physical chemists cited in the acknowledgement. These have not for the most part found widespread acceptance by chemical engineers, and it is not a simple matter to relate them to those which are more common. The means for making these inter-relations is provided in Chapter 3, but this reviewer did not find the treatment a convenient one to use. However, the definitions of mutual, self- and intra-diffusion coefficients in Chapter 1 are quite clear, and very useful as there has been much confusion about these terms.

Chapter 5 is, in this reviewer's opinion, highly useful, and a real strength of the book. The discussion of experimental techniques is detailed and practical, and also generally sound in terms of underlying theory. I do have a minor criticism in the discussion of Taylor dispersion in that the extensive literature on departures from Taylor's asymptotic theory is not referenced. Such departures can be important and may result from end effects or a variety of flow disturbances. This objection is, however, more than balanced by the strength of the discussion of errors in the use of light scattering. The authors have done much here to clear up longstanding controversies as to the significance of measurements made in concentrated solutions.

I found the organization of Chapters 6 through 8 awkward, but it may be that I did not take enough time to accommodate to it. It is clear that the authors have a prejudice which results in more attention to even doubtful theory than to useful empiricism. Thus they ignore many useful empirical and semi-empirical correlations totally. However, they do present a substantial amount of data and discuss it critically in the light of available theory, and these discussions should prove highly useful to many readers. They do seem more concerned with the experimental proof of the Onsager reciprocal relation than with the practical description of multicomponent diffusion problems, but in this they are constrained by the limited amount of practically useful information available.

On balance I expect to find this monograph a most welcome addition to my library, and a challenge to those like myself, with more applied tastes than the authors, to meet the above objections. I think this is the most authoritative source available in the area of diffusion, which is accessible to an engineering audience. □