

MIXTURES

The Theory of the
Equilibrium Properties of some
Simple Classes of Mixtures
Solutions and Alloys

E. A. GUGGENHEIM

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THE THEORY OF THE
EQUILIBRIUM PROPERTIES OF SOME
SIMPLE CLASSES OF MIXTURES
SOLUTIONS AND ALLOYS

BY

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OXFORD
AT THE CLARENDON PRESS

1952

PREFACE

My aim in this book has been to give an account of the application of statistical thermodynamics to certain models of solid, liquid, and gaseous mixtures. There has been no attempt to explore more than a small part of the wide field covered by the word 'mixture'. In fact the only models discussed are those so simple that theory can be applied to them quantitatively with the minimum of assumptions superposed on those implied in the models and can, moreover, be applied with the use of only elementary mathematics. In spite of the great simplicity of these models their study leads to problems sufficiently complicated to be interesting.

The models can be expected to be useful representations of only the simplest mixtures. In particular, mixtures containing electrolytes or highly polar molecules are entirely excluded from consideration. Comparison between theory and fact is limited by the scarcity of precise experimental measurements on the simpler systems. Where comparison is possible the result is nearly always surprisingly gratifying.

There is a clear need for more extensive and precise measurements of all the equilibrium properties of the simplest mixtures. If such research work is stimulated by the theories described, then this book will have served a useful purpose.

Here I should like to point out how much this subject owes to one of the founder-editors of this series, the late Sir Ralph Fowler. Although much of the theory has been developed since his death, there is scarcely a section which does not bear the imprint of ideas and techniques originated or inspired by him.

I have great pleasure in acknowledging my debt of gratitude to Dr. M. L. McGlashan for his invaluable assistance in preparing this book for the press. As well as contributing original work described in the book, he has read the manuscript, checked the formulae, prepared the diagrams, compiled the indexes, and corrected the proofs.

I am indebted to the Royal Society and to the North Holland Publishing Company for permission to copy certain diagrams.

E. A. G.

UNIVERSITY OF READING,

December 1951

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CLASSICAL THERMODYNAMICS OF MIXTURES

1.01. Introduction. Free energy

THE classical thermodynamics of mixtures is such a vast subject that an exhaustive treatment of it would require a book comparable in size to this one. No attempt will be made to give such a treatment here. We must rather be content with a brief summary of the fundamental principles and the most important formulae. The reader must go elsewhere for detailed derivations.

We shall in this book be concerned only with systems in complete thermal equilibrium, so that the temperature will always be uniform throughout the system. As long as the temperature is kept constant, that is to say under isothermal conditions, the most important thermodynamic function is the *free energy*, so named by Helmholtz and denoted by F . In any isothermal reversible process the increase in F , denoted by ΔF , is equal to the work done on the system; alternatively the decrease in F , denoted by $-\Delta F$, is equal to the work done by the system. Thus in reversible isothermal processes the free energy is analogous to the potential energy in reversible mechanical processes.

The particular kind of isothermal process which most concerns us here is that of the *mixing* of two or more substances. We shall denote by $-\Delta_m F$ the decrease in free energy when one mole of a mixture is formed from the constituent pure substances. A considerable part of this book will be concerned with the quantity $\Delta_m F$ called the *molar free energy of mixing*. It is important to know how this quantity is determined experimentally, but this can be explained more conveniently in § 1.05 after we have considered some other thermodynamic functions.

1.02. Independent variables

The state of a liquid mixture may be completely defined by specifying the absolute temperature T , the pressure P , and the composition of the liquid. This is moreover nearly always the most convenient manner of specification. The same choice of independent variables is appropriate to a solid mixture provided all stresses other than an isotropic pressure are excluded. For gaseous mixtures, on the other hand, it is sometimes more convenient to choose the volume V rather than the

pressure P as an independent variable. Since a much greater part of this book is devoted to liquids and solids than to gases, the set of independent variables T, P will be appropriate more often than the set T, V and therefore more detailed attention will be paid to the former.

The composition of a mixture is conveniently described by specifying the number n_r of moles of each species r . When we are interested only in the relative composition, but not in the total amount of a mixture, it is convenient to use the mole fractions x_r defined by

$$x_r = n_r / \sum_r n_r. \quad (1.02.1)$$

The mole fractions are thus not independent, being related by

$$\sum_r x_r = 1. \quad (1.02.2)$$

We shall be mostly concerned with binary mixtures for which (2) reduces to

$$x_1 + x_2 = 1. \quad (1.02.3)$$

In this case it will be convenient to simplify our notation by writing x instead of x_2 and $1-x$ instead of x_1 .

With this notation the molar free energy of mixing $\Delta_m F$ of a binary mixture is related to the molar free energy F_m of the mixture and the molar free energies F_1^0, F_2^0 of the two pure components by the definition

$$-\Delta_m F = (1-x)F_1^0 + xF_2^0 - F_m. \quad (1.02.4)$$

1.03. Thermodynamic potentials and fundamental equations

When the free energy F of any homogeneous phase is regarded as a function of the independent variables T, V, n_r , its partial differential coefficients with respect to the first two variables are given by the simple relations†

$$\partial F / \partial T = -S, \quad (1.03.1)$$

$$\partial F / \partial V = -P, \quad (1.03.2)$$

where S denotes the *entropy*. The partial differential coefficient of F with respect to each n_r is called the *chemical potential* of r and is denoted by μ_r . Thus

$$\partial F / \partial n_r = \mu_r. \quad (1.03.3)$$

Formulae (1), (2), and (3) may be combined to give

$$dF = -S dT - P dV + \sum_r \mu_r dn_r. \quad (1.03.4)$$

† The notation for all thermodynamic quantities is the same as used in the author's book *Thermodynamics* (1949), North-Holland Publishing Co., and conforms with the recommendations of the International Union of Physics (1948) and the International Union of Chemistry (1949). Derivations of all the required thermodynamic relations will be found in this or other standard text-books on chemical thermodynamics.

The free energy F is said to be the *thermodynamic potential* for the independent variables T , V , n_r , and formula (4) is called the *fundamental equation* for these variables.

Turning now to the more generally useful set of variables T , P , n_r , the relevant thermodynamic potential is the *Gibbs function* G defined by

$$G = F + PV, \quad (1.03.5)$$

and the fundamental equation for these variables is

$$dG = -S dT + V dP + \sum_r \mu_r dn_r. \quad (1.03.6)$$

Isothermal changes in G are closely related to *net work* defined as follows. The work done on a system plus the increase in the quantity PV is called the net work done on the system. Alternatively the work done by the system less the increase in the quantity PV is called the net work done by the system. In particular, if the pressure is kept constant then the net work done by the system may be defined as the work done by the system other than the work due to the change ΔV of its volume. With this definition of net work it follows from (5) that in a reversible isothermal process the decrease $-\Delta G$ of the Gibbs function is equal to the net work done by the system.

The *entropy* S has the property that in any infinitesimal reversible process the heat absorbed by the system is $T dS$. Consequently in any reversible isothermal process the heat absorbed is $T \Delta S$ or $\Delta(TS)$, where as usual the symbol Δ is used to denote the increase of any quantity during the process considered. If, on the other hand, we consider an isothermal process in which the pressure is maintained constant throughout, such a process being usually not reversible, then the heat absorbed is equal to the increase ΔH of the heat function H .

The functions G , S , and H are related by

$$H = G + TS, \quad (1.03.7)$$

$$S = -\frac{\partial G}{\partial T}, \quad (1.03.8)$$

$$H = G - T \frac{\partial G}{\partial T}. \quad (1.03.9)$$

Here and elsewhere when we use partial differential coefficients the independent variables are always T , P , n_r , unless the contrary is stated. It follows immediately that for an isothermal process in which the

initial and final pressures have specified values, usually but not necessarily the same, we have

$$\Delta H = \Delta G + T\Delta S, \quad (1.03.10)$$

$$\Delta S = -\frac{\partial}{\partial T}\Delta G, \quad (1.03.11)$$

$$\Delta H = \Delta G - T\frac{\partial}{\partial T}\Delta G. \quad (1.03.12)$$

The last formula is called the *Gibbs-Helmholtz relation*.

1.04. Partial molar quantities

The relations between partial molar quantities and the corresponding extensive property may be illustrated by the case where the property in question is the volume V . For the sake of brevity and simplicity we shall consider a mixture of only two components, 1 and 2. As usual we take as independent variables T , P , n_1 , n_2 . The *partial molar volumes* V_1 , V_2 are defined by

$$V_1 = \partial V / \partial n_1, \quad (1.04.1)$$

$$V_2 = \partial V / \partial n_2. \quad (1.04.2)$$

Incidentally the other partial differential coefficients of V are

$$\partial V / \partial T = \alpha V, \quad (1.04.3)$$

$$\partial V / \partial P = -\kappa V, \quad (1.04.4)$$

where α is the *coefficient of thermal expansion* and κ is the *isothermal compressibility*.

The total volume is related to the partial molar volumes by

$$V = n_1 V_1 + n_2 V_2. \quad (1.04.5)$$

When the composition of the mixture is varied at constant temperature and pressure the variations of the two partial molar volumes are inter-related by

$$n_1 dV_1 + n_2 dV_2 = 0 \quad (T, P \text{ const.}). \quad (1.04.6)$$

Applying the above formulae to a quantity of mixture containing in all one mole and denoting the mean molar volume by V_m , we have

$$V_m = (1-x)V_1 + xV_2, \quad (1.04.7)$$

$$\frac{\partial V_m}{\partial x} = V_2 - V_1, \quad (1.04.8)$$

$$(1-x)\frac{\partial V_1}{\partial x} + x\frac{\partial V_2}{\partial x} = 0 \quad (T, P \text{ const.}). \quad (1.04.9)$$

Precisely analogous formulae apply to any other extensive property

such as F , G , S , or H . In particular we see from (1.03.6) and the definition of partial molar quantities that

$$G_1 = \mu_1, \quad G_2 = \mu_2. \quad (1.04.10)$$

Consequently for variations in the composition of a binary mixture at constant temperature and pressure we have

$$(1-x) \frac{\partial \mu_1}{\partial x} + x \frac{\partial \mu_2}{\partial x} = 0 \quad (T, P \text{ const.}). \quad (1.04.11)$$

This important formula is called the *Gibbs-Duhem relation*.

Provided we keep to the independent variables T , P , n_1 , n_2 or T , P , x , then for each relation between extensive properties there is an analogous relation between the corresponding partial molar quantities. In particular as analogues of (1.03.7), (1.03.8), and (1.03.9) we have

$$H_1 = G_1 + TS_1, \quad H_2 = G_2 + TS_2, \quad (1.04.12)$$

$$S_1 = -\frac{\partial G_1}{\partial T}, \quad S_2 = -\frac{\partial G_2}{\partial T}, \quad (1.04.13)$$

$$H_1 = G_1 - T \frac{\partial G_1}{\partial T}, \quad H_2 = G_2 - T \frac{\partial G_2}{\partial T}. \quad (1.04.14)$$

By virtue of (10) we may rewrite these formulae as

$$H_1 = \mu_1 + TS_1, \quad H_2 = \mu_2 + TS_2, \quad (1.04.15)$$

$$S_1 = -\frac{\partial \mu_1}{\partial T}, \quad S_2 = -\frac{\partial \mu_2}{\partial T}, \quad (1.04.16)$$

$$H_1 = \mu_1 - T \frac{\partial \mu_1}{\partial T}, \quad H_2 = \mu_2 - T \frac{\partial \mu_2}{\partial T}. \quad (1.04.17)$$

1.05. Chemical potentials and absolute activities

We have already collected many of the most important formulae involving chemical potentials, but have not yet said anything about the physical significance of these quantities. The chemical potentials have two fundamental properties closely related to each other.

We have already drawn attention to the fact that the chemical potential is identical with the partial molar Gibbs function. We have also mentioned that in any reversible isothermal process the decrease in the Gibbs function is equal to the net work done by the system. It follows that if we consider the process of transferring one mole of the substance r reversibly and isothermally from a large quantity of one phase to a large quantity of another phase, then the decrease $-\Delta\mu_r$ in the value of the chemical potential μ_r is equal to the net work done

by the system. This is the first fundamental property of the chemical potential.

The second fundamental property of the chemical potential is the following. When two phases are at the same temperature the condition for equilibrium distribution of the substance r between the two phases is that the chemical potential μ_r should have the same value in both phases. This condition is valid even when the two phases are at different pressures, for example when separated by a semi-permeable membrane, provided always that they are at the same temperature.

The first fundamental property of the chemical potential enables us to relate the difference in chemical potential between two phases to experimentally determinable quantities. For the sake of simplicity we shall initially assume that the saturated vapour over each phase may with sufficient accuracy be treated as a perfect gas. It must be emphasized that this is an assumption relating only to the behaviour of the vapour; there is no restriction concerning the nature of the liquid or solid phases. The transfer of one mole of the substance r from a large quantity of a liquid or solid phase α to a large quantity of another liquid or solid phase β can in principle be performed reversibly and isothermally by what may be called an *isothermal three-stage distillation*. By means of pistons and appropriate semi-permeable membranes, which the interested reader can readily devise, the process can be performed in the following three stages:

- (a) Evaporate one mole of r from a large quantity of the phase α against a pressure equal to the saturated partial vapour pressure p_r^α of r in the phase α .
- (b) Expand or compress the one mole of vapour isothermally from the pressure p_r^α to a pressure equal to the saturated vapour pressure p_r^β of r in the phase β .
- (c) Condense the one mole into a large quantity of the phase β by applying a constant pressure p_r^β .

At all stages the temperature is supposed maintained constant by use of a suitable thermostat.

The work done by the system in the three stages when the vapour is treated as a perfect gas is as follows:

$$(a) \quad RT - p_r^\alpha V_r^\alpha, \quad (1.05.1)$$

$$(b) \quad RT \ln \frac{p_r^\alpha}{p_r^\beta}, \quad (1.05.2)$$

$$(c) \quad -RT + p_r^\beta V_r^\beta, \quad (1.05.3)$$

where R denotes the gas constant and V_r^α , V_r^β denote the partial molar volumes of r in the phases α , β respectively. By addition we find that the work done by the system is

$$RT \ln \frac{p_r^\alpha}{p_r^\beta} + (p_r^\beta V_r^\beta - p_r^\alpha V_r^\alpha). \quad (1.05.4)$$

It follows by definition that the net work done by the system is

$$RT \ln \frac{p_r^\alpha}{p_r^\beta}. \quad (1.05.5)$$

Thus for any two phases α , β at the same temperature we have

$$\mu_r^\alpha - \mu_r^\beta = RT \ln \frac{p_r^\alpha}{p_r^\beta}. \quad (1.05.6)$$

At this stage it is convenient to introduce another thermodynamic quantity λ_r called the *absolute activity* defined by

$$\mu_r = RT \ln \lambda_r. \quad (1.05.7)$$

Since λ_r and μ_r are so intimately and simply interrelated mathematically it is obviously unnecessary to use both. Nevertheless in practice it is often convenient to use λ_r rather than μ_r . The convenience of the *absolute activity* will reveal itself with use especially in statistical derivations.

Using the definition (7) we can rewrite (6) as

$$\frac{\lambda_r^\alpha}{\lambda_r^\beta} = \frac{p_r^\alpha}{p_r^\beta}. \quad (1.05.8)$$

Returning now to the second fundamental property of the chemical potential, we see that the condition that two phases α , β at the same temperature should be in equilibrium with respect to the substance r may be expressed in the mathematically equivalent forms

$$\mu_r^\alpha = \mu_r^\beta, \quad (1.05.9)$$

$$\lambda_r^\alpha = \lambda_r^\beta, \quad (1.05.10)$$

or provided only that the vapour may be treated as a perfect gas,

$$p_r^\alpha = p_r^\beta. \quad (1.05.11)$$

Even if the vapour may not be treated as a perfect gas these relations still hold good provided p_r is redefined as the *fugacity* instead of the partial vapour pressure. The fugacity may be regarded simply as a partial vapour pressure corrected for deviations from the behaviour of perfect gases. The manner of applying such corrections will be described in Chapter VIII.

Let us now consider a binary mixture of substances 1 and 2, and compare it with the two pure substances. We shall use the superscript 0 in symbols relating to either of the pure substances and shall omit superscripts from symbols relating to the mixture. We then have the following relations between several thermodynamic functions and the partial vapour pressures:

$$\mu_1^0 - \mu_1 = RT \ln \frac{\lambda_1^0}{\lambda_1} = RT \ln \frac{p_1^0}{p_1}, \quad (1.05.12)$$

$$\mu_2^0 - \mu_2 = RT \ln \frac{\lambda_2^0}{\lambda_2} = RT \ln \frac{p_2^0}{p_2}, \quad (1.05.13)$$

$$\begin{aligned} -\frac{\Delta_m G}{RT} &= (1-x) \ln \frac{\lambda_1^0}{\lambda_1} + x \ln \frac{\lambda_2^0}{\lambda_2} \\ &= (1-x) \ln \frac{p_1^0}{p_1} + x \ln \frac{p_2^0}{p_2}. \end{aligned} \quad (1.05.14)$$

The Gibbs-Duhem relation (1.04.11) may be rewritten in terms of absolute activities

$$(1-x) \frac{\partial \ln \lambda_1}{\partial x} + x \frac{\partial \ln \lambda_2}{\partial x} = 0 \quad (T, P \text{ const.}). \quad (1.05.15)$$

If we treat the vapour as a perfect gas, or alternatively if we let p denote fugacity instead of partial vapour pressure, we may replace (15) by

$$(1-x) \frac{\partial \ln p_1}{\partial x} + x \frac{\partial \ln p_2}{\partial x} = 0 \quad (T, P \text{ const.}). \quad (1.05.16)$$

This important formula is called the *Duhem-Margules relation*.

1.06. Useful formulae for liquids and solids

As we have emphasized at an early stage, the convenient choice of independent variables for liquid and solid phases is T , P , n_1 , n_2 , or T , P , x and therefore the appropriate thermodynamic potential is G not F . To avoid any possibility of confusion we have set out in full the most important formulae in terms of the chosen independent variables. Having done so, we may now point out that at ordinary pressures, for liquids at temperatures not too near the critical point and for solids, all terms in PV or VdP are entirely negligible. This is the case when the pressure is comparable to atmospheric, or is less. Thus, although it is important to remember that G , not F , is the thermodynamic potential for the independent variables T , P , yet the experimental or theoretical values of G are usually indistinguishable

from those of F . We may therefore usually, for liquids and solids, omit all terms in PV or $V dP$. We then obtain for binary mixtures, independently of the pressure provided it is not too great, such formulae as

$$dG = dF = -S dT + \mu_1 dn_1 + \mu_2 dn_2, \quad (1.06.1)$$

$$dG_m = dF_m = -S_m dT + (\mu_2 - \mu_1) dx, \quad (1.06.2)$$

$$(1-x) \frac{\partial \ln \lambda_1}{\partial x} + x \frac{\partial \ln \lambda_2}{\partial x} = 0 \quad (T \text{ const.}, P \text{ not too great}), \quad (1.06.3)$$

$$(1-x) \frac{\partial \ln p_1}{\partial x} + x \frac{\partial \ln p_2}{\partial x} = 0 \quad (T \text{ const.}, P \text{ not too great}). \quad (1.06.4)$$

To the same approximation there is no need to distinguish between the heat function H and the total energy $U = H - PV$.

To sum up, except when we are dealing with gases, we shall usually make no mention of pressure. The implied assumption is that the pressure is sufficiently small not to affect appreciably the values of the relevant thermodynamic functions. An exceptional case is that of osmotic equilibrium. The osmotic pressure Π , of a binary mixture in which the substance 1 is regarded as the solvent, is defined as the extra pressure which must be applied to the mixture to raise the partial vapour pressure of the solvent in the mixture to that of the pure solvent at ordinary low pressure. The osmotic pressure is related to the partial vapour pressure of the solvent by the formula

$$\Pi = \frac{RT}{V_1} \ln \frac{p_1}{p_1^0}, \quad (1.06.5)$$

where p_1 , p_1^0 denote partial vapour pressures over the solution and the pure solvent respectively *at the same external pressure*. V_1 as usual denotes the partial molar volume of the solvent in the mixture, and is here assumed indistinguishable from the molar volume V_1^0 of the pure solvent.

1.07. Activity coefficients

We have mentioned that the absolute activities of the two components depend on the composition so as to be interrelated by the Duhem-Margules relation

$$(1-x) \frac{\partial \ln \lambda_1}{\partial x} + x \frac{\partial \ln \lambda_2}{\partial x} = 0 \quad (T \text{ const.}). \quad (1.07.1)$$

The simplest solution of this equation has the form

$$\lambda_1 = \lambda_1^0(1-x), \quad \lambda_2 = \lambda_2^0 x. \quad (1.07.2)$$

The same relations may be expressed in terms of partial vapour pressures, or strictly fugacities,

$$p_1 = p_1^0(1-x), \quad p_2 = p_2^0x. \quad (1.07.3)$$

As we shall see in Chapter III, the simplest kind of mixture which exists in fact satisfies the above relations. Such mixtures are called *ideal*. Whereas ideal mixtures are the exception rather than the rule, they provide a conveniently useful standard with which to compare other real mixtures. For this purpose it is expedient to introduce *activity coefficients* f_1, f_2 defined by

$$\lambda_1 = \lambda_1^0(1-x)f_1, \quad \lambda_2 = \lambda_2^0xf_2, \quad (1.07.4)$$

$$\text{or} \quad p_1 = p_1^0(1-x)f_1, \quad p_2 = p_2^0xf_2. \quad (1.07.5)$$

It then follows by substitution of (4) into (1) that the variations with composition of the activity coefficients of the two species are inter-related by

$$(1-x)\frac{\partial \ln f_1}{\partial x} + x\frac{\partial \ln f_2}{\partial x} = 0 \quad (T \text{ const.}). \quad (1.07.6)$$

The introduction of activity coefficients of course gives us no quantitative information concerning the properties of the mixture until their values have been determined experimentally. Their introduction is merely a convenience and a worthwhile one because the same activity coefficients enter into all the equilibrium relations of the mixture. We have already seen that the partial vapour pressures of the two components are given by (5). By comparison with (1.06.5) we see that the osmotic pressure Π (for osmotic equilibrium with respect to the species 1) is given by

$$\Pi = \frac{RT}{V_1} \ln \frac{1}{(1-x)f_1}. \quad (1.07.7)$$

We shall now record without proof the formulae relating to equilibrium between the liquid solution and the pure solid phase of one of the components. For equilibrium at the temperature T between the solution and the solid phase consisting of the pure substance 1 the relation is

$$\ln \frac{1}{(1-x)f_1} = \frac{\Delta_f H_1^0}{R} \left(\frac{1}{T} - \frac{1}{T_1^0} \right), \quad (1.07.8)$$

where T_1^0 denotes the equilibrium temperature for the pure liquid 1 and $\Delta_f H_1^0$ denotes the molar heat of fusion of the pure substance 1. To be more precise $\Delta_f H_1^0$ denotes an average value of this quantity over the temperature range T to T_1^0 , but usually the variation of the