

Studies on the Chemical Theory of Solutions.

Part I.

By

K. Ikeda, *Rigakuhakushi.*

CONTENTS.

INTRODUCTION.

CHAPTER I. THE IDEAL SOLUTION.

- § 1. General nature of the ideal solution.
- § 2. Equilibrium between gaseous and liquid phases.
(a) Vapour pressure at a constant temperature. (b) Isothermal distillation. (c) Boiling point of an ideal solution.
- § 3. Equilibrium between the ideal solution and pure solids.
(a) Isothermal relations. (b) Relation between the temperature of fusion and the composition of the solution.
- § 4. Equilibrium between the ideal solution and the ideal solid solution.
(a) Isothermal relations. (b) Relation between the temperature and the composition of the two phases.

CHAPTER II. QUASI-IDEAL SOLUTIONS WITH ONE ASSOCIATED COMPONENT.

- § 1. Associated liquids.
(a) Homogeneous equilibrium. (b) Vapour tension of an associated liquid. (c) Acetaldehyde and paraldehyde. (d) Physical properties of associated liquids.
- § 2. Quasi-ideal solution with a normal and an associated component.
(a) Homogeneous equilibrium. (b) Equilibrium between a gaseous and a liquid phase. (1) Vapour tension at a constant temperature. (2) The system acetone-ethyloxyde. (3) Boiling point under constant pressure. (c) Equilibrium between a liquid and a solid phase. (1) The solid is the normal component. (2) The solid is the associated component.
- § 3. Systems with one associated and two normal components.
(a) Homogeneous equilibrium. (b) Equilibrium between a gaseous and a liquid phase. (c) Equilibrium between a liquid and a solid phase. (1) Solubility curves. (2) Fusion surfaces.

Introduction.

The theory of dilute solutions, with which the name of VAN T'HOFF is most prominently associated, has been one of the chief agencies in the rapid development of physical chemistry in the last two decades. But its applicability is by its very nature limited, and for further progress a more general theory, such as will enable us to treat quantitatively problems of solutions of any composition, must be worked out. This want has been generally felt, and attempts to meet it have been made by various physicists and chemists.

Among these the elaborate molecular theory of binary mixtures by VAN DER WAALS stands preëminent, and has led to many investigations theoretical as well as experimental. But his theory is bound up with the equation that bears his name, and requires complicated mathematical apparatus in solving even apparently simple problems. For systems in which chemical reactions take place, or in which the number of components exceeds two, the difficulties become so great that no noteworthy progress has as yet been achieved in these directions.

A simpler method of procedure might perhaps lead to the goal more quickly. It has been demonstrated by the investigations of DAHMS, HARTMANN, LECHATLIER, LINEBARGER, SCHROEDER, VAN LAAR, YOUNG, ZAWIDZKI, and others, that there are some solutions in which the quantitative relations of the heterogeneous equilibria are remarkably simple. These approximate pretty closely to what has been called the "ideal solution." But the majority of the solutions hitherto studied show more or less marked deviations from these simple relations. Are we to con-

sider these simple cases as accidental and try to establish a theory which would embrace the manifoldness of the phenomena in one general consideration? Or are we to look at these simplest relations as normal and try to account for the deviations by introducing appropriate hypotheses? The teaching of the history of chemistry leaves us no doubt on this point. The anomalous behaviour of vapours, which appeared at first to endanger the universal validity of the gas laws, led to the establishment of the *chemical* hypothesis of association and dissociation, a hypothesis which has proved so fruitful and assisted in no small degree in the development of rational views on chemical affinity. Again the anomalies of the salt solutions with respect to the theory of the dilute solution have found their natural explanation in the *chemical* hypothesis of electrolytic dissociation, under whose banner physical chemistry has achieved so many conquests. What then could be more natural than to assume the simple and regular behaviour of certain solutions as normal and to consider the deviations from such as due to reversible chemical reactions taking place in the solution? And as the manifoldness of chemical reactions is inexhaustible, the resources of this hypothesis must be so too. It is indeed not difficult to imagine that most of the complex relations actually observed could be accounted for in this way. The theory of solution based on such a hypothesis may be called *chemical* in contrast to such a physical theory as that of VAN DER WAALS.

In working out the consequences of particular hypothesis there is always danger of becoming one-sided and losing sight of other possibilities. Yet for the first attempts it would be better not to be too circumspect, lest one should be lost in the maze of the variety of things which must be taken into considera-

tion at the same time. Had the propounder of the theory of electrolytic dissociation sought for all the various factors which might have some bearing upon the deviations from the simple laws of the dilute solution and attempted to interweave these into his fundamental conceptions, he would certainly have produced a more general theory, but it is very doubtful whether he could have achieved so much for the real progress of the science. The present studies have been prosecuted in the same spirit, directness and simplicity of treatment having been striven for rather than generality and rigour. The deviations from the ideal behaviour are considered to be caused by chemical changes alone. In this way it is hoped that the general behaviour of solutions may be made comprehensible, and more particularly that the quantitative relations of heterogeneous equilibria may be elucidated. Conversely it may also be expected that the state of chemical equilibrium in concentrated solutions will be deduced from the study of heterogeneous equilibria. This application, when it can really be made, will prove to be of considerable importance to various branches of chemistry.

It may, however, be urged that in the liquid state the individual properties of the components and the influences of their mutual actions, which are also of a specific nature, are predominant, and that the deviations from the ideal behaviour caused by these factors may be much more considerable than is the case with rarefied gases or dilute solutions, so that quite anomalous relations may obtain without any chemical change taking place. This objection is of course irrefutable. But in a great many cases where chemical reactions are avowedly excluded, close approximation to the ideal behaviour has been observed. We have therefore some reason to suppose that the deviations

caused by the physical factors are in general not so great that the deviations called forth by considerable chemical changes become entirely indistinguishable. At any rate we may deduce various types of homogeneous and heterogeneous equilibria by assuming various chemical reactions in the solution, and compare them with observed cases. Exact numerical agreement is of course not to be looked for, but more or less close approximation should be found in many cases, especially when the components are not of a too divergent nature.

When the chemical theory has been worked out to a certain extent and established on the sure foundation of observation, it will be time to take the physical factors into consideration and construct a more complete theory of solution.

CHAPTER I.

THE IDEAL SOLUTION.

§ 1. The General Nature of the Ideal Solution.

The behaviour of the ideal solution in various relations must be investigated in the first place because it forms the foundation of the present study. By the ideal solution is meant a homogeneous liquid mixture in which the following two conditions are fulfilled:

1. The volume of the solution is the sum of the volumes of the components (in the liquid state) under the same pressure and at the same temperature.

2. The energy of the solution is the sum of the energies of the components (in the liquid state) under the same pressure and at the same temperature.

These conditions may be expressed by the following equations :

$$V = n_1 v_1 + n_2 v_2 + \dots, \dots\dots\dots(1)$$

$$E = n_1 \varepsilon_1 + n_2 \varepsilon_2 + \dots, \dots\dots\dots(2)$$

where V and E are the volume and energy of the solution, n_1, n_2, \dots are the number of mols (gramme-molecules), v_1, v_2, \dots the so-called molecular volumes, and $\varepsilon_1, \varepsilon_2, \dots$ energies per mol of the components $\mathfrak{S}_1, \mathfrak{S}_2, \dots$. These conditions must hold at all temperatures and pressures.

The first condition is what is called by VAN DER WAALS the law of AMAGAT. While the law of DALTON is a so-called "Grenzgesetz" to which the gas mixtures approximate the more closely the greater the rarefaction, the law of AMAGAT has a wide range of application, gases under high pressures being known to obey it in some cases. It is quite probable that it would hold, at least approximately, for most gaseous mixtures in which chemical reaction is excluded, because even liquids form solutions with extremely small change of volume when they are unasociated.

The second condition is also fulfilled at least approximately by these liquid mixtures, because the heat disturbances observed on mixing are mostly quite small, being in some cases apparently nil. Hence it is also highly probable that gases under pressures, high or low, should fulfill the condition more or less closely.

When these conditions are satisfied, the chemical potentials of the components have a very simple form just as in a mixture of ideal gases :

$$\left. \begin{aligned} \mu_1 &= z_1 + RT \ln C_1 \\ \mu_2 &= z_2 + RT \ln C_2 \\ &\dots\dots\dots \end{aligned} \right\} \dots\dots\dots (3)$$

where $\mu_1, \mu_2, \dots\dots\dots$ are the molecular chemical potentials, $z_1, z_2, \dots\dots\dots$ the molecular thermodynamic potentials in the isolated state, and $C_1, C_2, \dots\dots\dots$ the molar fractions (the thermodynamic or numerical concentrations) of the components $\mathfrak{S}_1, \mathfrak{S}_2, \dots\dots\dots$

The relation expressed by (3) can be readily deduced from (1) and (2). From the latter we see that the work gained by mixing must be proportional to absolute temperature, and from (1) that it is independent of pressure. When the temperature is sufficiently raised and the pressure sufficiently lowered the mixture as well as the components is in a state approaching that of ideal gases and the work obtainable by reversible mixing of the components is equal to

$$-n_1 RT \ln C_1 - n_2 RT \ln C_2 - \dots\dots\dots,$$

which is proportional to the absolute temperature. The work obtainable by the formation of the solution can therefore be represented by the same expression. Z , the thermodynamic potential (or the available energy at constant temperature and pressure) of the solution must be equal to the sum of the available energies of the components minus the work obtainable during the formation of the solution. Hence

$$Z = n_1 z_1 + n_2 z_2 + \dots\dots\dots + n_1 RT \ln C_1 + n_2 RT \ln C_2 + \dots\dots\dots,$$

which on differentiation with respect to $n_1, n_2, \dots\dots\dots$ gives:

$$\begin{aligned} \mu_1 &= \frac{\partial Z}{\partial n_1} = z_1 + RT \ln C_1 \\ \mu_2 &= \frac{\partial Z}{\partial n_2} = z_2 + RT \ln C_2 \\ &\dots\dots\dots \end{aligned}$$

In the foregoing deductions it is not necessary to make any assumption as to the molecular weights of the components in the liquid state.

It is enough to use those in the gaseous state. But the molecular weight of a gaseous substance is determined theoretically by the amount of work obtainable by its diffusion or expansion. As substances can be made to pass continuously from the gaseous to the liquid state, and as the work obtainable by the interdiffusion of the components is identical in both, the molecular weights of the components in the liquid state must be considered to remain the same as in the gaseous state. In fact all the components which mix with one another with very small changes of volume and energy are without exception unassociated liquids.

From the amount of work obtainable by reversible mixing we can readily calculate the strength of the osmotic pressure exerted on a semipermeable septum if we assume the liquids to be incompressible. When the mixing is accomplished by means of an osmotic apparatus having as many semipermeable pistons as there are components, then the work must be

$$n_1\pi_1v_1 + n_2\pi_2v_2 + \dots = -n_1RT \ln C_1 - n_2RT \ln C_2 - \dots$$

where π_1, π_2, \dots are the osmotic pressures exerted by the solution on the pistons allowing the passage of $\mathfrak{S}_1, \mathfrak{S}_2, \dots$ respectively. As n_1, n_2, \dots can be varied independently of one another, it follows

$$\begin{aligned} \pi_1v_1 &= -RT \ln C_1 \\ \text{or} \quad \pi_1 &= \frac{-RT \ln C_1}{v_1} \end{aligned}$$

which of course gives VAN T'HOFF's relation for the cases in which C_1 approaches unity.

The physical properties of the ideal solutions are mostly of an additive nature. That the heat capacity and the compressibility must belong to this category follows from conditions (1) and (2). Refraction of light calculated according to the formula of GLADSTONE and DALE or that of LORENZ and LORENTZ agrees in some cases almost exactly with the supposition. Other optical

properties such as the absorption of light or the rotation of the plane of polarisation are probably also additive. The molecular surface tension of such solutions has been shown to be of the same nature by RAMSAY and ASTON (*Zeits. physik. Chem.*, **15**, 89; 1894). No doubt with the extension of exact measurements of various properties such examples would be greatly increased.

§ 2. The Equilibrium between Gaseous and Liquid Phases.

(a) Vapour Pressure at a Constant Temperature.

In the following the gas phases are assumed to be so rarefied that the gas laws are applicable without restriction. In such case the relations obtaining are remarkably simple.

The chemical potential of the components in the liquid phase may, under the circumstances, be considered as constant at a constant temperature and independent of pressure. The chemical potential of the components in the gas phase varies of course with pressure. For the component \mathfrak{S}_1 it is

$$\mu_1' = z_1' + RT \ln P + RT \ln C_1', \dots\dots\dots(4)$$

where z_1' is the molecular thermodynamic potential of the isolated component in the gaseous state at the temperature T and under the unit pressure, while C_1' is the molar fraction of the component in the gas phase.

If the isolated component \mathfrak{S}_1 has the vapour pressure P_1 at the temperature T_1 then we have

$$z_1 = z_1' + RT \ln P_1.$$

When the solution is in equilibrium with its vapour

$$\mu_1 = \mu_1',$$

hence

$$z_1' + RT \ln P_1 + RT \ln C_1 = z_1' + RT \ln P + RT \ln C_1'$$

or

$$C_1 P_1 = C_1' P = p_1 \dots\dots\dots(5)$$

in which p_1 denotes the partial pressure of \mathfrak{S}_1 in the gas phase. A similar consideration applies to other components. This important relation can be expressed in the following words:

At a given temperature the partial pressure of a component in the gas phase is equal to the vapour tension of the component in the pure state multiplied by the molar fraction of the component in the liquid phase.

The total pressure P is of course equal to the sum of the partial pressures.

In a binary system we have

$$C_2 = 1 - C_1$$

and
$$p_1 + p_2 = P.$$

If we take the molar fraction C_1 as abscissa and the pressure as ordinate we get the diagram shown in Fig. 1. As the curves of the partial pressures p_1 and p_2 are straight lines, that of the total pressure is also a straight line.

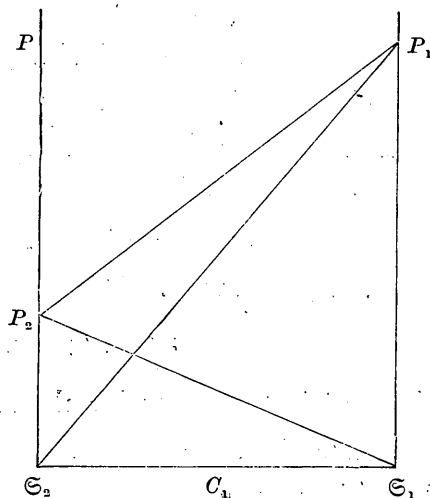


Fig. 1.

The fact that the composition-pressure curve is a straight line for a binary ideal solution was first established by F. GUTHRIE (Phil. Mag., V, 18, 517; 1884). He found that contraction on mixing of two liquids is generally accompanied by the evolution of heat, and expansion of volume by the absorption of heat. He also observed that in

the former case the curves of total vapour pressure are convex to the axis of composition, while in the latter case they are concave. He reasoned from these facts that for a mixture in the formation of which neither a change of volume nor of heat takes place the vapour tension curve must be a straight line. He found his anticipation nearly realised in the mixture of ethyl chloride and iodide.

The results of the experimental studies of LINEBARGER, HARTMANN, LEHFELD, and ZAWIDZKI have been incorporated in the standard work of ROOZEBOOM (*Heterogene Gleichgewichte*, II, 21), hence it is not necessary to discuss them here. In all the cases where the curves of total as well as of partial pressure are straight lines the components are substances known, by the method of surface tension, to be unassociated. Some mixtures of presumably normal liquids give curves which are not quite straight, but the curvatures are mostly quite small. Doubtless many liquids usually supposed to be normal are associated to a slight extent.

According to VAN DER WAALS the conditions necessary for straight vapour pressure curves are the following:

(a) The heat of the evaporation of the mixture is the sum of the heats of the evaporation of the components.

(b) The critical pressures of the two components are equal.

That (a) is the consequence of (2) is evident, while (b) has no direct relation with (1). KOHNSTAMM (*Zeits. physik. Chem.*, **36**, 52; 1901) tried to verify the condition (b), but could not reach any satisfactory result owing to the inaccuracy of the data on critical pressure.

According to YOUNG (*Journ. Chem. Soc.*, **83**, 45; 1903) the chemical similarity of the components is one of the conditions

for straight vapour pressure curves. Yet ZAWIDZKI has found the mixture of benzene and carbon tetrachloride to have such curves. If the idea of chemical similarity could be applied to such cases, it would be too indefinite to be of much value as a criterion. Yet there seems to be some truth in YOUNG's assertion, because chemically allied substances mix with one another mostly without much change of energy or of volume.

In a ternary system the vapour pressures, total as well as partial, are represented by planes as shown in Fig. 2, while the surface of the total pressure has the form of a sail spread between three points, when the composition is that of the gas phase. The plain and the curved surfaces of the total pressure are represented by the following equations:

$$P = C_1 P_1 + C_2 P_2 + C_3 P_3$$

$$\frac{1}{P} = \frac{C'_1}{P_1} + \frac{C'_2}{P_2} + \frac{C'_3}{P_3}$$

where C'_1 , C'_2 , C'_3 are the molar

fractions of the components in the gas phase, and P_1 , P_2 , P_3 are the vapour pressures of the pure components at the given temperature.

It is quite clear that these equations can be extended and applied to the ideal system of any number of components.

There seem to be some solid solutions whose vapour pressure

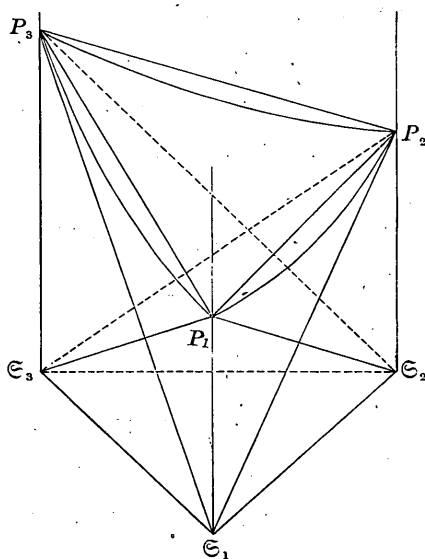


Fig. 2.

corresponds tolerably closely to that of an ideal solution. For example, SPERANSKI (Zeits. physik. Chem., 51, 55; 1905) found that the vapour pressure curve of the solid solution of p-dichlorobenzene and p-dibromobenzene was very nearly a straight line throughout the whole range of his experiment, which extended up to 45% mol dibromobenzene. The temperature was varied between 40.3°C. and 66.1°C. without any noticeable influence on the result. This mixture was studied by KÜSTER (Zeits. physik. Chem., 51, 235; 1905) who employed a dynamical method for the measurement of the small vapour pressures. He found that the curve of the partial pressure of p-dichlorobenzene is nearly a straight line, while that of p-dibromobenzene is concave towards the axis of composition and has a maximum. If the data were exact they would be of considerable interest, because they contradict the relation of DUHEM-MARGULES which ought to be universally applicable.

(b) *Isothermal Distillation.*

Fractional distillation is one of the most important operations employed in separating the various components from mixtures. It is daily practised in laboratories and factories, but the exact quantitative theory of the process remains to be developed. This is no doubt due to the lack of insight into the exact relation between temperature, pressure, and the compositions of the phases, gaseous and liquid. For ideal solutions such insight is given and a part of the problem can be solved with comparative ease. For example, take the subject of isothermal distillation. In this case we not only have to determine how the compositions of the distillate and the residue vary with pressure, but we must also calculate the quantity of the distillate.

To begin with a binary mixture, let the initial conditions of the solution be as follows :

N_1 = number of mols of \mathfrak{S}_1

N_2 = „ „ „ „ \mathfrak{S}_2

P_0 = vapour pressure.

Then we have

$$P_0 = \frac{N_1}{N_1 + N_2} P_1 + \frac{N_2}{N_1 + N_2} P_2;$$

hence if the initial pressure be given, the composition can be calculated by the following equation

$$\frac{N_1}{N_1 + N_2} = \frac{P_0 - P_2}{P_1 - P_2};$$

and if the initial weight of the solution be known, N_1 and N_2 can be determined.

At any moment let the pressure be P and the number of mols of the components in the residue be n_1 and n_2 respectively. Then in the infinitesimal evaporation the following relation must hold :

$$dn_1 : dn_2 = C_1' : C_2'$$

But by the equation (5) we have .

$$C_1' = \frac{P_1}{P} \frac{n_1}{n_1 + n_2}, \quad C_2' = \frac{P_2}{P} \frac{n_2}{n_1 + n_2};$$

hence

$$\frac{1}{P_1} \frac{dn_1}{n_1} = \frac{1}{P_2} \frac{dn_2}{n_2},$$

which on integration becomes

$$\frac{1}{P_1} \ln \frac{n_1}{N_1} = \frac{1}{P_2} \ln \frac{n_2}{N_2} \dots\dots\dots (6)$$

This expression combined with the equation

$$\frac{n_1}{n_1 + n_2} = \frac{P - P_2}{P_1 - P_2}$$

suffices to determine the values of n_1 and n_2 . In the distillate there are $N_1 - n_1$ mols of the first component, and $N_2 - n_2$ mols of the second. In this way the compositions and quantities of the distillate and residue are determined in terms of pressure, and the problem is solved.

In the ternary system the composition of the residue suffers a definite course of change during the process of isothermal distillation. This can be represented by a curve in the triangular diagram. The nature of this curve was first investigated by SCHREINEMAKERS (*Zeits. physik. Chem.*, 36, 422; 1901) and is called the distillation curve. So long as the temperature is kept constant the composition of the residue can vary only along this curve. How this comes to pass can be briefly explained in the following manner.

Let g in Fig. 3 represent the composition of the liquid phase and g' that of the gas phase in equilibrium with it. As the distillation goes on the composition of the residue will be displaced a little in the direction of the line $g'g$ according to the well known theorem of the ternary mixture. Hence gg' is the tangent of the curve, and thus the direction of the curve is determined. After a certain amount of liquid has been distilled, the liquid phase will have the composition f , while that of the

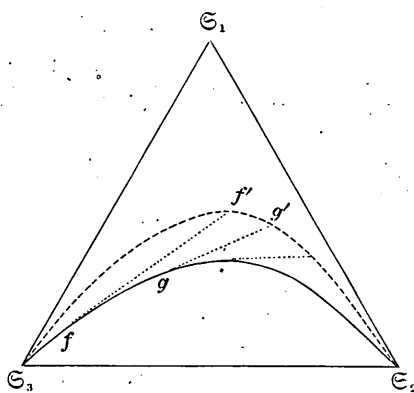


Fig. 3.

gas phase will be f' , and the curve will proceed in the direction $f'f$, etc., etc.

In the case of an ideal solution we have

$$p_1 = C_1'P = C_1P_1$$

$$p_2 = C_2'P = C_2P_2$$

$$p_3 = C_3'P = C_3P_3$$

and

$$P = C_1P_1 + C_2P_2 + C_3P_3.$$

Hence

$$C_1' = \frac{C_1P_1}{C_1P_1 + C_2P_2 + C_3P_3}$$

$$C_2' = \frac{C_2P_2}{C_1P_1 + C_2P_2 + C_3P_3}$$

As the tangent to the distillation curve passes through the point C_1, C_2 as well as the point C_1', C_2' we have

$$\frac{dC_2}{dC_1} = \frac{C_2 - C_2'}{C_1 - C_1'} = \frac{C_2\{C_1P_1 + C_2P_2 + (1 - C_1 - C_2)P_3 - P_2\}}{C_1\{C_1P_1 + C_2P_2 + (1 - C_1 - C_2)P_3 - P_1\}} \dots\dots(7)$$

Which may also be written

$$\frac{dC_2}{dC_1} = \frac{C_2(P - P_2)}{C_1(P - P_1)}.$$

Suppose the first component to be the most volatile and the second component to be the least volatile of the three, then

$$P - P_2 > 0, \quad P - P_1 < 0;$$

and as both C_1 and C_2 are necessarily positive

$$\frac{dC_2}{dC_1} < 0.$$

In other words C_2 must decrease as C_1 increases. The curve of isothermal distillation has therefore the form represented by $\mathfrak{S}_1A\mathfrak{S}_2$, etc., Fig. 4. When there is but little \mathfrak{S}_1 in the solution $\frac{dC_2}{dC_1}$ must be very large, and when $C_1 = 0$ the curve coincides

with the axis $\mathfrak{S}_3 \mathfrak{S}_2$. Hence if there is much of \mathfrak{S}_3 in the original solution the curve will have a form like $\mathfrak{S}_1 C \mathfrak{S}_2$. On the contrary, when there is but little of \mathfrak{S}_3 the curve will have a form like $\mathfrak{S}_1 B \mathfrak{S}_2$. If $C_3 = 0$,

$$(P - P_2) : (P - P_1) = -C_1 : C_2$$

and
$$\frac{dC_2}{dC_1} = -1,$$

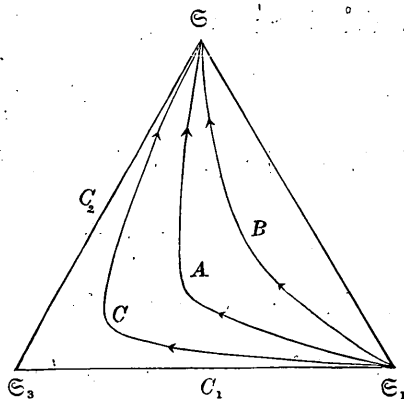


Fig. 4.

so that the curve coincides with the axis $\mathfrak{S}_2 \mathfrak{S}_1$.

The equation (7) can be written

$$\frac{dC_2}{dC_1} = -\frac{C_2 \{ (P_1 - P_2) C_1 + (P_3 - P_2) (1 - C_1 - C_2) \}}{C_1 \{ (P_1 - P_2) C_2 + (P_1 - P_3) (1 - C_2 - C_3) \}},$$

which can be readily transformed into

$$(P_2 - P_3) \frac{dC_1}{C_1} + (P_3 - P_1) \frac{dC_2}{C_2} - (P_1 - P_2) \frac{dC_1 + dC_2}{1 - C_1 - C_2} = 0.$$

On integration we get

$$C_1^{P_2 - P_3} C_2^{P_3 - P_1} C_3^{P_1 - P_2} = \mathfrak{S}_1^{P_2 - P_3} \mathfrak{S}_2^{P_3 - P_1} \mathfrak{S}_3^{P_1 - P_2} \dots (8)$$

where \mathfrak{C}_1 , \mathfrak{C}_2 , and \mathfrak{C}_3 are the initial molar fractions of the components. This is the equation of the curve of isothermal distillation.

The composition and the quantity of the residue during the process of isothermal distillation of a ternary mixture can be calculated in exactly the same manner as in the case of a binary system. We have

$$dn_1 : dn_2 : dn_3 = C_1' : C_2' : C_3'$$

which becomes by (5)

$$\frac{1}{P_1} \frac{dn_1}{n_1} = \frac{1}{P_2} \frac{dn_2}{n_2} = \frac{1}{P_3} \frac{dn_3}{n_3}.$$

This can be readily integrated to

$$\frac{1}{P_1} \ln \frac{n_1}{N_1} = \frac{1}{P_2} \ln \frac{n_2}{N_2} = \frac{1}{P_3} \ln \frac{n_3}{N_3} \dots\dots\dots (a)$$

We have also the relation

$$P = \frac{n_1}{n_1 + n_2 + n_3} P_1 + \frac{n_2}{n_1 + n_2 + n_3} P_2 + \frac{n_3}{n_1 + n_2 + n_3} P_3 \dots\dots\dots (b)$$

These three equations of (a) and (b) are sufficient to determine the values of n_1 , n_2 , and n_3 .

(c) *The Boiling Point of an Ideal Solution.*

As explained under (a) the relation between the total pressure on one hand and the vapour pressures of the pure components and composition on the other is very simple at a constant temperature. Hence if the vapour pressure of the components be given as a function of temperature, the relation between boiling point and composition can be readily ascertained. Now let the vapour pressure of the components be expressed by:

$$P_1 = \varphi_1(T), \quad P_2 = \varphi_2(T), \quad \text{etc.}$$

and let \mathfrak{P} be the constant pressure under which the solution boils, then we have

$$p_1 + p_2 + \dots\dots = C_1 \varphi_1(T) + C_2 \varphi_2(T) + \dots\dots = \mathfrak{P} \dots\dots\dots (9)$$

The variation of the vapour pressure of each component with the temperature is given by the equation of CLAPEYRON-CLAUSIUS:

$$\frac{\partial \ln P_1}{\partial T} = \frac{q_1}{RT^2}, \quad \frac{\partial \ln P_2}{\partial T} = \frac{q_2}{RT^2}, \quad \text{etc.}$$

where q_1, q_2, \dots represent the molecular heat of evaporation. The limitations to which the application of the equations are subject are too well known to be mentioned in this place. q_1, q_2, \dots diminish with rising temperatures, but the exact form of the function is not known. Within a short range of temperature, say thirty to fifty degrees, and particularly in the region where the vapour pressure is not very large, q_1, q_2, \dots may be considered constant without causing much error.¹⁾ The equations can then be integrated into

$$P_1 = e^{a_1 - \frac{q_1}{RT}}, \quad P_2 = e^{a_2 - \frac{q_2}{RT}}, \quad \text{etc.} \dots\dots\dots (A)$$

where a_1, a_2, \dots are constants. In cases where the differences between the boiling points are not great the equation (9) can be written

$$C_1 e^{a_1 - \frac{q_1}{RT}} + C_2 e^{a_2 - \frac{q_2}{RT}} + \dots\dots = \mathfrak{P} \dots\dots\dots (10)$$

TROUTON'S law simplifies the matter considerably. According to this law the ratio between the molecular heat of evaporation and the absolute temperature of the boiling point is constant for various substances. This has been verified for many unassociated liquids under ordinary atmospheric pressure. But there is no doubt that the law is also applicable to cases in which the pressure is considerably smaller. Only the ratio must increase with decreasing pressure. Thus under ordinary atmospheric pressure,

1) Otherwise we have the usual equation with more than two constants in the form $\ln P = A - \frac{B}{T} + C \ln T + DT + \dots\dots\dots$. But then the constants can no longer be determined with necessary definiteness from empirical data, because slight experimental errors cause considerable shifting between the values of the constants. Hence the approximate equation is employed advisedly, not only to lessen mathematical complicaey, but also to make the deductions more definite.

$$\frac{q_1}{RT_1} = \frac{q_2}{RT_2} = \dots\dots\dots = 10.9 \text{ nearly,}$$

while under a pressure of 200 m.m. mercury the following values have been found:

Substance.	Ether.	Iodobenzene.	Benzene.	Carbon tetrachloride.
$\frac{q}{RT}$	12.9	12.6	12.5	12.7

The values of q have been calculated by means of the CLAPEYRON-CLAUSIUS equation from the vapour pressures determined by RAMSAY and YOUNG.

As $\frac{q_1}{RT_1}$, $\frac{q_2}{RT_2}$,..... are equal, a_1 , a_2 ,..... must also be equal, the numerical value depending on the unit of pressure employed. Hence if we put

$$\frac{q_1}{RT_1} = \frac{q_2}{RT_2} = \dots\dots\dots = b$$

then

$$a_1 = a_2 = \dots\dots\dots = b + \ln \mathfrak{P}.$$

The equations (A) then become

$$P_1 = e^{a_1 - \frac{q_1}{RT}} = \mathfrak{P} e^{b \left(1 - \frac{T_1}{T}\right)},$$

$$P_2 = e^{a_2 - \frac{q_2}{RT}} = \mathfrak{P} e^{b \left(1 - \frac{T_2}{T}\right)},$$

$$\dots\dots\dots,$$

in which T_1 , T_2 ,..... are the only constants characteristic of the components. The equation (10) now reduces to

$$C_1 e^{b \left(1 - \frac{T_1}{T}\right)} + C_2 e^{b \left(1 - \frac{T_2}{T}\right)} + \dots\dots\dots = 1 \dots\dots\dots(11)$$

When C_1 , C_2 ,..... are given, the boiling point T of the solution can be calculated by this equation. But it is only for a binary

mixture that the composition can be determined from the boiling point. For solutions with more than two components the equation becomes indeterminate.

YOUNG and FORTEY (Journ. Chem. Soc., 83, 45; 1905) tested the applicability of the equation (9) to various binary solutions approximating more or less closely to the ideal solution. Of these the mixture of chloro- and bromobenzene satisfied conditions (1) and (2) most closely, and they found that the boiling point of the mixture could be represented quite well by equation (9). For $\varphi(T)$ they employed Biot's formula. The calculation with equation (11) is of course much simpler, while the agreement is nearly as good, as is shown in the following table:

Boiling point.	132.0°	136.75°	142.16°	148.16°	156.0°
Molar fraction of C_6H_5Br	0	.2501	.5000	.7364	1.000
Ditto calculated	—	.253	.498	.739	—

The differences between the observed and calculated molar fractions do not exceed 3%, which corresponds to about .05° in the measurement of temperature, and seems to be nearly equal to the limit of error. The value of b employed in the calculation is 10.9, and is nearly equal to the mean value.

If only one component be volatile, then

$$\mathfrak{P} = p_1 = C_1 P_1$$

or

$$C_1 \varphi_1(T) = \mathfrak{P}$$

In the cases where the simple equation (A) is sufficed

$$C_1 e^{a_1 - \frac{q_1}{RT}} = e^{a_1 - \frac{q_1}{RT_1}}$$

or taking the logarithm

$$\ln C_1 = \frac{q_1}{R} \left(\frac{1}{T} - \frac{1}{T_1} \right). \dots\dots\dots(12)$$

This equation is inapplicable to cases in which C_1 is very small, because then P_1 will be very large and cannot be well expressed by the simple equation (A). But in other cases C_1 can be calculated from the boiling point by equation (12).

If we express the sum of molar fractions of all the involatile components by C , then $C_1 = 1 - C$, and we get

$$-\ln(1 - C) = \frac{q_1}{RTT_1} (T - T_1). \dots\dots\dots(13)$$

$T - T_1$ is what is called the elevation of the boiling point, and increases with increasing C . Equation (13) might well be employed for the determination of the molecular weight, etc. in the cases where the solution is not dilute but approximately ideal. When the solution is very dilute, C is very small in comparison with unity and we may write C instead of $-\ln(1 - C)$, and T_1^2 instead of TT_1 , and equation (13) passes into

$$C = \frac{q_1}{RT_1^2} (T - T_1)$$

which is the well known equation of VAN T'HOFF.

§ 3. Equilibrium between Ideal Solutions and Pure Solids.

The problems of the equilibrium between solid and liquid phases are full of interest. Yet the treatment of them has hitherto been almost exclusively qualitative, the exceptions being those cases which could be solved by the theory of dilute solutions,

and some other simple cases which will be mentioned further on. In the case of ideal solutions it is quite easy to establish general quantitative relations and these may serve as the norm in the investigation of actual cases. Even with the ideal solutions there are so many problems that the discussion must be restricted to the more important ones. The influence of pressure has not been taken into consideration because it is in general quite insignificant.

(a) *Isothermal Relations.*

Equation (3) demonstrates the applicability of the law of mass action to ideal solutions of any composition. It is indeed very inconvenient to use the idea of spatial concentration in the case of concentrated solutions and this must be replaced by that of molar fraction. GULDBERG and WAAGE reached the conclusion that the active mass of a pure solid substance is constant at a constant temperature. From this standpoint the relations of solubility at a constant temperature can be readily surveyed and described.

When the solid phase has the composition $\mathfrak{S}_{1\nu_1}\mathfrak{S}_{2\nu_2}\dots\dots$ the composition of the solution which is in equilibrium with the solid must satisfy the following equation:

$$C_1^{\nu_1} C_2^{\nu_2} \dots\dots = K \dots\dots\dots(14)$$

$\nu_1, \nu_2, \dots\dots$ are the so called molecular coefficients or exchange numbers (HELM). K is a function of temperature and pressure. But as the influence of the latter is generally very slight K may be considered to be constant when the temperature is constant.

Equation (14) which represents the law of mass action in

this case, can be deduced in the following manner. Let Z'' be the thermodynamic potential of one mol of the solid phase, then,

$$Z'' = \nu_1 \mu_1 + \nu_2 \mu_2 + \dots,$$

because one mol of the solid phase produces on melting ν_1 mols of \mathfrak{S}_1 , ν_2 mols of \mathfrak{S}_2 , etc., and in the state of equilibrium there could be neither gain nor loss of available energy on fusion. But as has been established in § 1,

$$\left. \begin{aligned} \mu_1 &= z_1 + RT \ln C_1 \\ \mu_2 &= z_2 + RT \ln C_2 \\ &\dots \end{aligned} \right\} \dots \dots \dots (3)$$

hence

$$Z'' = \nu_1 z_1 + \nu_2 z_2 + \dots + \nu_1 RT \ln C_1 + \nu_2 RT \ln C_2 + \dots,$$

and as Z'' , z_1 , z_2 , \dots can be considered to be nearly independent of pressure, they are constant at a constant temperature. Therefore

$$\nu_1 \ln C_1 + \nu_2 \ln C_2 + \dots = \ln K = \text{const.}$$

which is equation (14) in logarithms.

Equation (14) admits of some interesting deductions. For this purpose we will put

$$\left. \begin{aligned} \frac{\nu_1}{\nu_1 + \nu_2 + \dots} &= \gamma_1 \\ \frac{\nu_2}{\nu_1 + \nu_2 + \dots} &= \gamma_2 \\ &\dots \end{aligned} \right\} \dots \dots \dots (15)$$

and

$$\gamma_1^{\nu_1} \gamma_2^{\nu_2} \dots = x \dots \dots \dots (16)$$

γ_1 , γ_2 , \dots are the molar fractions of \mathfrak{S}_1 , \mathfrak{S}_2 , \dots in the melt

of the pure compound, and it is quite clear that

$$K \begin{matrix} < x \\ > 0 \end{matrix}$$

For example, for the binary compound $\mathfrak{S}_1\mathfrak{S}_2$ K is less than $\frac{1}{4}$ and for the compound $\mathfrak{S}_{1_2}\mathfrak{S}_2$

K is less than $\frac{4}{27}$.

When the solid is a component, we have by (14),

$$C_1 = K.$$

In a binary system this is represented by a point on the line of composition (Fig. 5, A). In a ternary system the equation is represented by a straight line parallel to one of the axes of composition (Fig. 5, B); while in a quaternary system, by a plane parallel to one of the planes of the tetrahedron of composition (Fig. 5, C).

When the solid is a binary compound, then we have

$$C_1^{y_1} C_2^{y_2} = K.$$

In the case of a binary system this becomes

$$C_1^{y_1} (1 - C_1)^{y_2} = K.$$

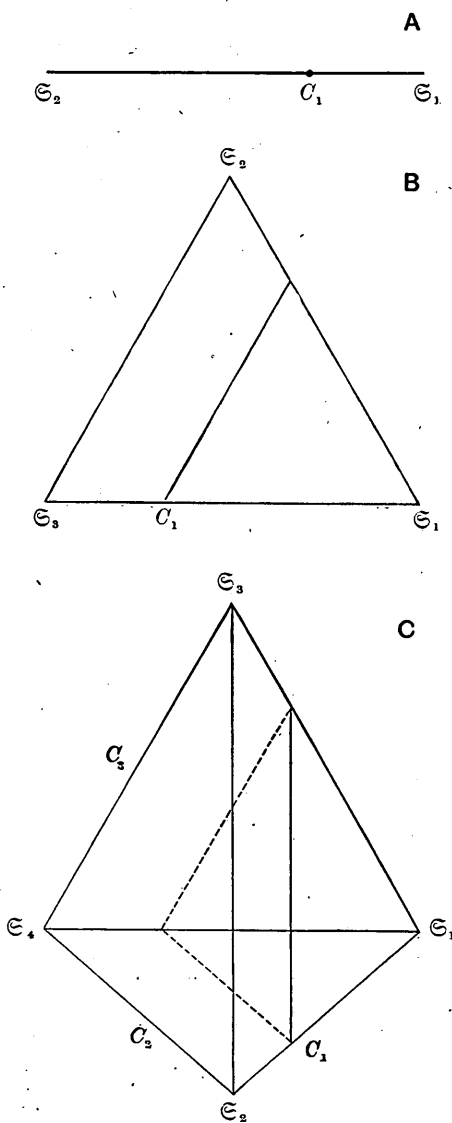


Fig. 5.

There are two positive values of C_1 which satisfy the equation, and these are represented by two points on the line of composition, situated on the opposite sides of the point $C_1 = \gamma$ (Fig. 6, A). In systems with more than two components we have the additional condition

$$C_1 + C_2 < 1.$$

This, combined with the foregoing equation, gives a solubility curve of the form shown in Fig. 6, B for a ternary system. γ is a point at which

$$C_1 = \frac{\nu_1}{\nu_1 + \nu_2}.$$

In a quaternary system the surface of solubility is a ruled surface whose general form is represented by Fig. 6, C.

When the solid is a ternary compound $\mathfrak{S}_{1\nu_1}\mathfrak{S}_{2\nu_2}\mathfrak{S}_{3\nu_3}$, the curve of solubility in a ternary system has the form shown in Fig. 7, A. The symmetry of the curve depends of course on the symmetry relations between the coefficients ν_1 , ν_2 , and ν_3 .

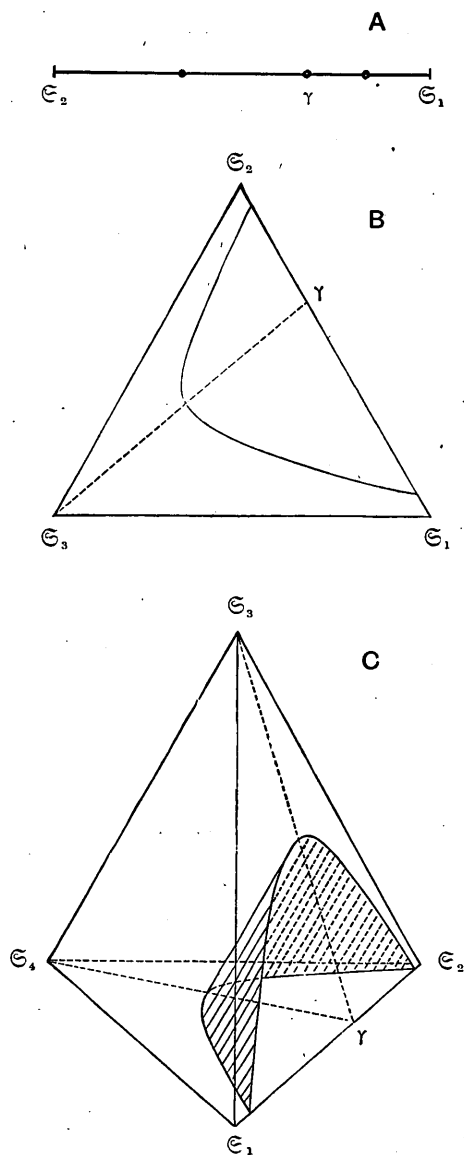


Fig. 6.

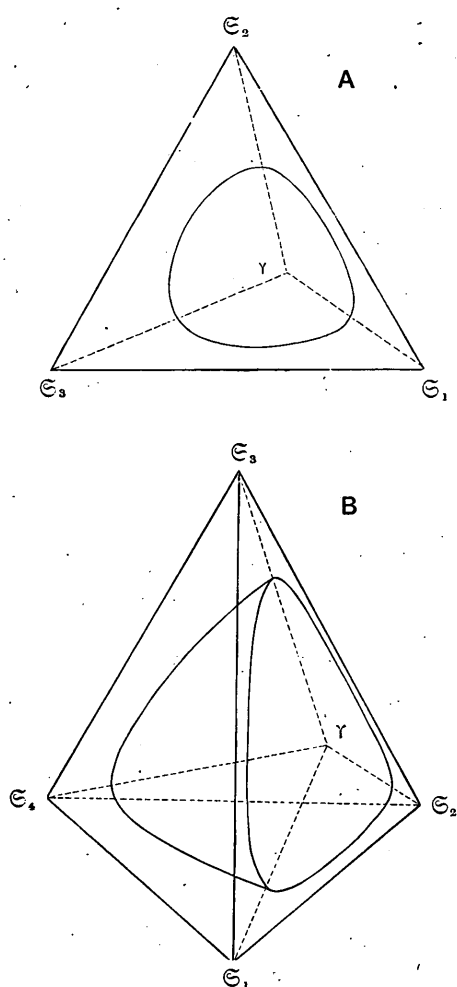


Fig. 7.

having the form shown in Fig. 8.

It must be remembered that no compound exists in the ideal solution itself, because the formation of a com-

In a quaternary system the surface of solubility has the form represented by Fig. 7, B. When the molar fraction of ϵ_4 exceeds a certain value, the product $C_1^{v_1} C_2^{v_2} C_3^{v_3}$ can no longer be equal to K , but falls below it. Hence the surface must have a maximum point, for which the value of ϵ_4 is the maximum. This point lies on the straight line connecting the points ϵ_4 and γ .

When the solid is a quaternary compound, the surface of solubility will be a closed one,

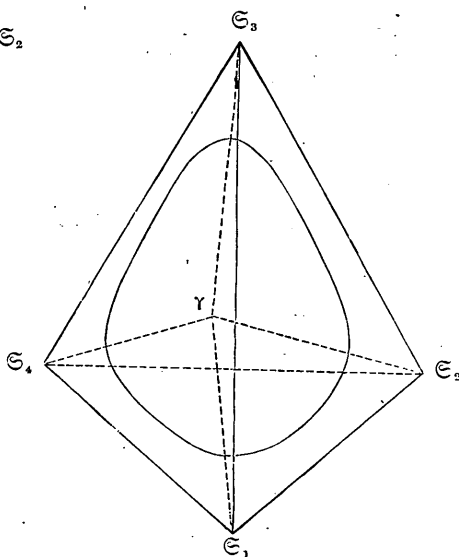


Fig. 8.

pound would be accompanied by changes of energy and volume, and would thus be incompatible with conditions (1) and (2). The equilibrium between a solid compound and an ideal solution is therefore comparable to that between ammonium carbamate and the gaseous mixture of ammonia and carbon dioxide. As the difference of densities between a solid and a liquid is not so great as between a solid and a gas it is quite probable that more or less of the compound exists in the liquid solution also. Hence the curves and surfaces corresponding exactly to the equation

$$C_1^{v_1} C_2^{v_2} \dots = \text{const.}$$

will rarely be met with in actual cases. The foregoing considerations may, however, be of some value as establishing the normal types. On the other hand the straight line and the plane of solubility corresponding to the equation

$$C_1 = K$$

will be often met with.

(b) *The Relation between the Temperature of Fusion and the Composition of the Solution.*

That no sharp distinction can be made between fusion and dissolution of solids was pointed out long ago by GUTHRIE (Phil. Mag., V, 18, 118; 1884), who exemplified his view by the system potassium nitrate—water, and it has now become a current opinion. Hence in speaking of a binary system the terms fusion curve and solubility curve have identical meanings. Yet it is more convenient to have one term which denotes isothermal

relations and another which denotes the relation between the temperature and the composition of the solution which is in equilibrium with a solid phase. The terms solubility curve and solubility surface have been employed to denote isothermal relations in the foregoing passages. The terms fusion curve and fusion surface will be employed to denote the relation between temperature and composition.

The ideal fusion curve of a binary system has already been repeatedly a subject of study. LE CHATELIER and SCHROEDER chose the RAOULT-VAN T'HOFF equation for vapour pressure as the starting point of their investigation, while DAHMS and VAN LAAR employed the method of thermodynamic potential. The result arrived at is the same and is represented by the equation :

$$\ln C_1 = \frac{Q_1}{R} \left(\frac{1}{T_1} - \frac{1}{T} \right), \dots\dots\dots(17)$$

in which Q_1 is the molecular heat of the fusion of the component \mathfrak{S}_1 , and T_1 is the temperature of the fusion of the same. The form is identical with that of equation (12), the only difference being caused by the different signs of q_1 and Q_1 . Detailed discussion is given by ROOZEBOOM in his standard work (*Heterogene Gleichgewichte*, II, 274). The three conditions stipulated for the validity of the equation are :

- I. The concentration C_1 shall be the so called thermodynamical one, i.e. the molar fraction.
- II. The solid component shall separate out pure.
- III. Q_1 shall be independent of temperature.

The necessity of the second condition is evident. The cases in which this is not fulfilled will be treated in the next section.

The third condition is an assumption which does not stand in any necessary connection with the conception of the ideal solution developed in the present study. TAMMANN has observed that the heat of fusion is nearly constant along the fusion curve of one component system (the temperature-pressure curve). And as the heat of mixing is nil in the case of ideal solutions the assumption seems to be quite plausible. But the specific heats of the same component as solid and liquid are in general not equal. Hence the condition will rarely be fulfilled exactly. Still for the cases in which the temperature range is somewhat limited the assumption may be admitted as a convenient approximation. Two conditions out of the three being thus extraneous to the conception of an ideal solution, there remains only the first condition to be examined. Excepting the cases in which the gas pressure or the osmotic pressure are avowedly taken into consideration, the idea of molecular weight is generally rather vague in thermodynamical discussions, and the molecular weights employed in calculating C_1 may well be those in the gaseous state and not those in the liquid state. This is often explicitly stated in the deduction of the laws of dilute solutions. Hence the first condition does not coincide with condition (1) or (2), and it is doubtful whether the three conditions given by ROOZEBOOM suffice to establish equation (17). On the other hand DAHMS mentions conditions (1) and (2) explicitly.

The relation between the temperature and the composition of an ideal solution which is in equilibrium with a solid phase, either a component or a compound, can be deduced in the following manner. The equation (see page 7),

$$\begin{aligned} Z'' &= \nu_1 \mu_1 + \nu_2 \mu_2 + \dots \\ &= \nu_1 z_1 + \nu_2 z_2 + \dots + RT(\nu_1 \ln C_1 + \nu_2 \ln C_2 + \dots), \end{aligned}$$

is of course valid for any temperature. On differentiating with respect to T we get:

$$\frac{\partial Z''}{\partial T} = \nu_1 \frac{\partial z_1}{\partial T} + \nu_2 \frac{\partial z_2}{\partial T} + \dots + RT \frac{\partial \ln K}{\partial T} + R \ln K,$$

where K has the meaning defined by equation (14), but is no longer constant as the temperature is considered variable. From the definition of Z'' , z_1 , z_2 , it follows:

$$\frac{\partial Z''}{\partial T} = -S'', \quad \frac{\partial z_1}{\partial T} = -S_1, \quad \frac{\partial z_2}{\partial T} = -S_2, \quad \text{etc.}$$

where S'' is the molecular entropy of the solid compound $\mathfrak{S}_{1\nu_1} \mathfrak{S}_{2\nu_2} \dots$, and S_1 , S_2 , are the molecular entropies of the components in the liquid state. We have therefore,

$$RT \frac{\partial \ln K}{\partial T} = \nu_1 S_1 + \nu_2 S_2 + \dots - S'' - R \ln K.$$

But as $-RT \ln K$ is nothing but the maximum work obtainable by mixing the liquid components in the proportion necessary for the formation of one mol of the compound, we have the following relation:

$$\nu_1 S_1 + \nu_2 S_2 + \dots - S'' - R \ln K = \frac{Q}{T},$$

where Q is the molecular heat of fusion of the compound. The foregoing differential equation reduces therefore to:

$$\frac{\partial \ln K}{\partial T} = \frac{Q}{RT^2}, \quad \dots \dots \dots (18)$$

a form which is identical to the reaction isochor of VAN T'HOFF.

This equation can be integrated when Q is given as function of temperature. Let us assume as an approximation, that Q is independent of temperature. Then

$$\ln \frac{K}{z} = \frac{Q}{R} \left(\frac{1}{T_1} - \frac{1}{T} \right), \dots (19)$$

where z stands for the value of K in the melt of the pure compound, according to equation (16), and T_1 stands for the melting point of the compound.

When the solid is a component, then

$$z = 1$$

and $K = C_1,$

and equation (19) assumes the form (17), which is applicable to systems of any number of components.

Several cases in which equation (17) represents the actual course of fusion curves in binary systems have been

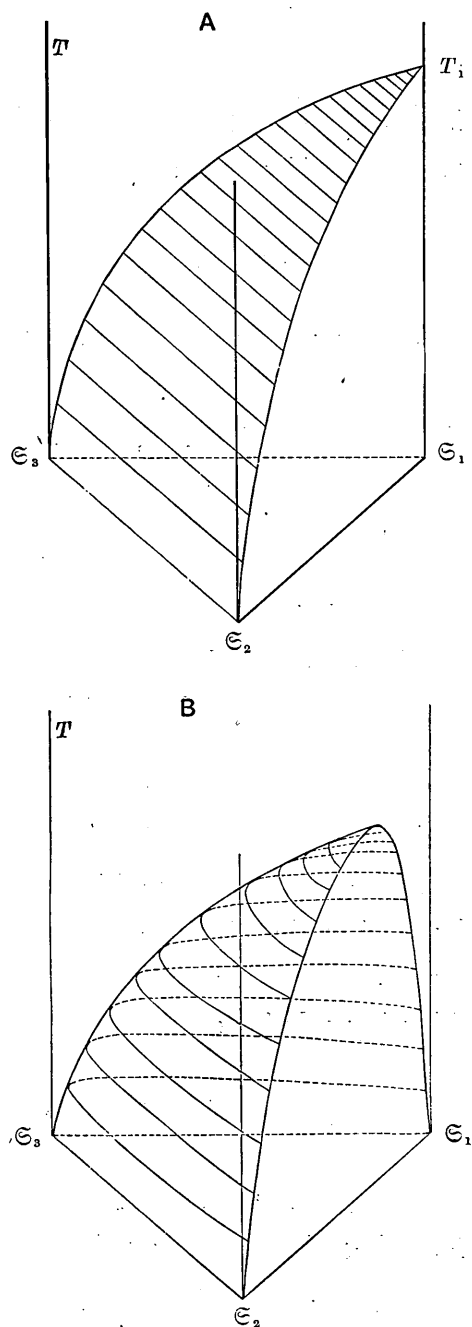


Fig. 9.

studied by the authors mentioned above. The form of the curve has been discussed by VAN LAAR in detail. On the other hand graphical representations of the general features of the fusion curves and surfaces may be of some interest although they do not bring out anything new.

Fig. 9, A represents the fusion surface of a component in a ternary system, while Fig. 9, B and C represent the fusion surfaces of a binary and a ternary compound.

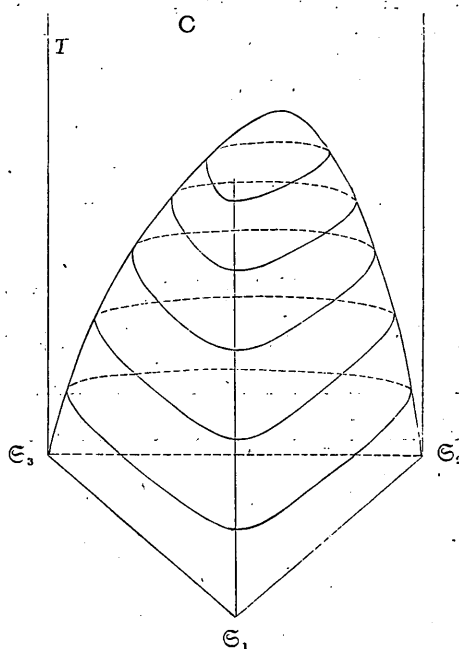


Fig. 9.

§ 4. The Equilibrium between an Ideal Liquid and an Ideal Solid Solution.

It is probable that, in some cases, at least, conditions (1) and (2) are satisfied by solid solutions. For example, RETGER observed in several cases of isomorphous mixtures, that the volume was equal to the sum of the volumes of their components. And if these conditions are fulfilled, we may apply equation (3) in the discussion of equilibria into which such solid solutions enter. In the present section the equilibrium between an ideal solid and an ideal liquid solution will be considered. As the solid phase is supposed by the very conditions not to contain any compound, the problem is so far simplified. The equilibrium

between a solid component or a solid compound and an ideal solid solution may be treated just in the same manner as in the foregoing section.

(a) *Isothermal Relations.*

The relation between the compositions of an ideal liquid and an ideal solid solution at a constant temperature can be found in the following manner. Let μ_1 and μ_1'' be the molecular chemical potential of the first component in the liquid and the solid phase respectively. Then we have by equation (3)

$$\mu_1 = z_1 + RT \ln C_1$$

and

$$\mu_1'' = z_1'' + RT \ln C_1''$$

where z_1'' and C_1'' denote the corresponding quantities for the solid solution, as z_1 and C_1 for the liquid phase. In the case of equilibrium

$$\mu_1 = \mu_1'';$$

hence

$$\ln \frac{C_1}{C_1''} = \frac{z_1'' - z_1}{RT} \dots \dots \dots (20)$$

The supposition that z_1'' as well as z_1 is independent of pressure may be looked upon as a close approximation as long as the variation of pressure is not very considerable. Under this assumption we have

$$\frac{C_1}{C_1''} = r_1 = \text{const.} \dots \dots \dots (21)$$

for a constant temperature. Similarly

$$\frac{C_2}{C_2''} = r_2 = \text{const.}$$

.....

r_1, r_2, \dots are all positive numbers greater or less than unity; but they can not all be greater or less than unity, because this would lead to incompatibilities. For example, in a binary system

$$\frac{C_1}{C_1''} = r_1 \dots\dots\dots (A)$$

and

$$\frac{1-C_1}{1-C_1''} = \frac{1-r_1 C_1''}{1-C_1''} = r_2 \dots\dots\dots (B)$$

Hence if r_1 be greater than unity then r_2 must be less than unity. These two equations (A) and (B) determine the values of C_1 and C_1'' . In other words, the composition of the two phases must have fixed values, which is in accordance with the phase rule.

For a ternary system we have

$$\frac{C_1}{C_1''} = r_1, \quad \frac{C_2}{C_2''} = r_2, \quad \frac{1-C_1-C_2}{1-C_1''-C_2''} = r_3,$$

from which we get

$$\left. \begin{aligned} C_2'' &= \frac{r_3-1}{r_3-r_2} + \frac{r_1-r_3}{r_3-r_2} C_1'' \\ C_2 &= \frac{r_2(r_3-1)}{r_3-r_2} + \frac{r_2(r_1-r_3)}{r_1(r_3-r_2)} C_1 \end{aligned} \right\} \dots\dots\dots (22)$$

The former of these two equations represents the solubility curves with respect to the composition of the solid phase, and

the latter with respect to that of the liquid. These curves are straight lines, and the angle which one of them makes with the axis of C_1 must have the same sense as the angle which the other line makes with the same axis. Fig. 10 represents these lines, with the conjugated points connected by straight lines.

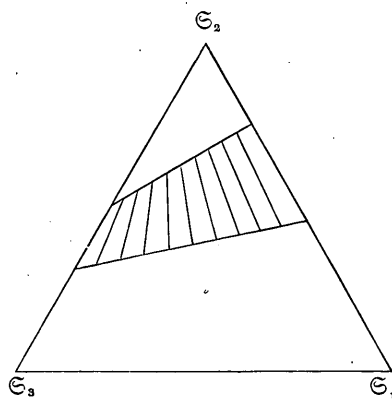


Fig. 10.

(b) *The Relation between the Temperature and the Composition of the two Phases.*

Differentiating equation (20) with respect to T ,

$$RT \frac{\partial \ln \frac{C_1}{C_1''}}{\partial T} = (S_1 - S_1'') - R \ln \frac{C_1}{C_1''},$$

$$RT \frac{\partial \ln \frac{C_2}{C_2''}}{\partial T} = (S_2 - S_2'') - R \ln \frac{C_2}{C_2''},$$

.....

where S_1'' , S_2'' , etc. are the molecular entropies of the solid components. The right sides of the equations represent the increase of entropy when one mol of each component passes from the solid to the liquid phase. When r_1 , r_2 , are not very large or very small the heat absorbed when one mol of \mathfrak{S}_1 , \mathfrak{S}_2 , passes from the solid to the liquid solution is very nearly equal to the heat of fusion q_1 , q_2 ,, and we have

$$\frac{\partial \ln \frac{C_1}{C_1''}}{\partial T} = \frac{q_1}{RT^2}$$

$$\frac{\partial \ln \frac{C_2}{C_2''}}{\partial T} = \frac{q_2}{RT^2}$$

.....

Assuming q_1, q_2, \dots to be independent of temperature and integrating, we get:

$$C_1 = C_1'' e^{\frac{q_1}{R} \left(\frac{1}{T_1} - \frac{1}{T} \right)}$$

$$C_2 = C_2'' e^{\frac{q_2}{R} \left(\frac{1}{T_2} - \frac{1}{T} \right)}$$

.....

But as

$$C_1 + C_2 + \dots = 1,$$

and

$$C_1'' + C_2'' + \dots = 1,$$

we have

$$\left. \begin{aligned} C_1'' e^{\frac{q_1}{R} \left(\frac{1}{T_1} - \frac{1}{T} \right)} + C_2'' e^{\frac{q_2}{R} \left(\frac{1}{T_2} - \frac{1}{T} \right)} + \dots &= 1, \\ C_1 e^{\frac{q_1}{R} \left(\frac{1}{T} - \frac{1}{T_1} \right)} + C_2 e^{\frac{q_2}{R} \left(\frac{1}{T} - \frac{1}{T_2} \right)} + \dots &= 1, \end{aligned} \right\} \dots (23)$$

relations quite analogous to that represented by equation (11). Equations (23) represent the fusion curves, surfaces, etc. according to the number of the components.

CHAPTER II.

QUASI-IDEAL SOLUTIONS WITH ONE ASSOCIATED COMPONENT.

In the systems, which we have been considering in the preceding chapter, it has been assumed that chemical changes do not take place in the homogeneous phases; because if the state of isomeric or polymeric equilibrium of the independent components be disturbed on mixing them, or if they enter into combination with one another, energy- and volume-change must necessarily occur and conditions (1) and (2) will not be satisfied. Yet, that the chemical species¹⁾ could be mixed without such changes is not excluded, provided the chemical reactions were checked. In order to make the matter more readily conceivable we may suppose with LUTHER (Zeits. Electrochem., 12, 87; 1906) that a negative catalyser has been added to the chemical species before mixing. This does not of course affect the chemical potentials. Hence if the chemical species are miscible without volume- and energy-change, the chemical potentials have the values given by equation (3). Such a solution, in which reversible chemical reactions take place but whose volume and energy are equal to the sums of the respective quantities of the component chemical species, we propose to call a quasi-ideal solution. It can be readily imagined that actual solutions which approximate more or less closely to the quasi-ideal solution will be far more numerous than those which approximate to the ideal

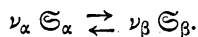
1) The term "chemical species," which has been employed by some older writers but has lately almost gone out of use, may be employed to denote distinct chemical entities real or imaginary. It is preferable to the term "molecular species."

solution. Of all sorts of quasi-ideal solutions, the one with only one associated component is the simplest, and such we undertake to study in the present chapter. When there are two or more associated components, the formation of compounds between them is quite probable and the subject threatens to become rather intricate, and the theoretical discussion runs the risk of losing itself in a labyrinth of hypotheses unless there is a goodly store of exact experimental materials. This will explain the singular limitation imposed on the subject of the present chapter. The subject will be treated in the order of complexity, i.e. according to the number of components in the system.

§ 1. Associated Liquids.

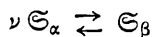
(a) *Homogeneous Equilibrium.*

The chemical reactions in a one component system can be represented generally by the equation



When $\nu_{\alpha} = \nu_{\beta}$ the reaction is an isomeric change, when $\nu_{\alpha} \geq \nu_{\beta}$ it is a polymeric change, and when $\nu_{\beta} = 1$ the reaction is called association. Such a system has been called by ROOZEBOOM pseudounary.

In an associated liquid any number of reactions of the type



may take place. But in order to simplify the discussion we will suppose that there is only one such reaction.

When an associated liquid is a quasi-ideal solution, then

$$\left. \begin{aligned} \mu_{\alpha} &= z_{\alpha} + RT \ln C_{\alpha}, \\ \mu_{\beta} &= z_{\beta} + RT \ln C_{\beta}. \end{aligned} \right\} \dots\dots\dots (24)$$

As long as the variation of pressure is not very large we may assume z_α and z_β to be functions of temperature alone.

In the case of equilibrium

$$\nu \mu_\alpha = \mu_\beta$$

so that for a constant temperature

$$\frac{C_\alpha^\nu}{C_\beta} = \frac{C_\alpha^\nu}{1-C_\alpha} = e^{\frac{z_\beta - \nu z_\alpha}{RT}} = \mathfrak{K} = \text{const.} \dots\dots\dots(25)$$

\mathfrak{K} in this equation is what is called the equilibrium coefficient.

The ratio between the mean molecular weight of the liquid and the molecular weight of \mathfrak{S}_α has been called by RAMSAY and SHIELDS the degree of association. If we express this ratio by ξ , then

$$\xi = \nu - (\nu - 1) C_\alpha = 1 + (\nu - 1) C_\beta \dots\dots\dots(26)$$

The experimental determination of ξ presents considerable difficulties. RAMSAY and SHIELDS attempted to evaluate it from the temperature coefficient of the molecular surface energy, but with only partial success. RAMSAY afterward modified the mode of calculation and his results are widely accepted. But there is a serious doubt about the entire method, because it is based upon the assumption that the composition of the surface film is the same as that of the liquid mass. For mixtures of chemical species of nearly equal volatility the assumption may hold. But in the case of an associated liquid the component chemical species must have a very different volatility. The more volatile species will tend to accumulate in the surface film, because its molecular surface energy will be considerably less than that of the less volatile species, whose critical temperature must be assumed to be much higher than that of the other.

Even in the cases where ξ is given \mathfrak{K} can not be determined at once, because ν is generally unknown. But ν is in general a small integer, and we are often able to deduce or infer its value from various experimental data.

The variation of \mathfrak{K} with the temperature is expressed by the equation

$$\frac{\partial \ln \mathfrak{K}}{\partial T} = \frac{\mathfrak{Q}}{RT^2}$$

where \mathfrak{Q} is the heat of reaction for ν mols of \mathfrak{S}_α . As it is quite probable that the heat capacity of \mathfrak{S}_β is not very different from that of $\nu \mathfrak{S}_\alpha$, we may as an approximation, assume \mathfrak{Q} to be independent of temperature, then

$$\ln \mathfrak{K} = \frac{\mathfrak{Q}}{R} \left(\frac{1}{\mathfrak{T}} - \frac{1}{T} \right) \dots\dots\dots(27)$$

where \mathfrak{T} is the temperature at which \mathfrak{K} becomes unity. This temperature may be called the *equipoise point* of the reaction and is characteristic of the homogeneous equilibrium just as the boiling point, melting point, or eutectic point is characteristic of the respective heterogeneous equilibrium. For such reactions as $2 \text{O}_3 \rightleftharpoons 3 \text{O}_2$ or $2 \text{H}_2\text{O} \rightleftharpoons 2 \text{H}_2 + \text{O}_2$ the equipoise point is very high, while for such reactions as $2 \text{SCl}_2 \rightleftharpoons \text{S}_2\text{Cl}_2 + \text{Cl}_2$ it is relatively low. When the given temperature is far from the equipoise point we may say that the chemical species on the right or the left side of the equation are stable against the species on the other side according as \mathfrak{Q} , the heat of reaction, is positive or negative.

(b) *Vapour Tension of an Associated Liquid.*

If we assume that the chemical species \mathfrak{S}_α and \mathfrak{S}_β taken

separately present the vapour pressures π_α and π_β respectively at the given temperature, the vapour pressure of the associated liquid will be

$$P = C_\alpha \pi_\alpha + (1 - C_\alpha) \pi_\beta. \dots\dots\dots(28)$$

C_α can be determined as a function of temperature from equation (27), when ν , Ω , and \mathfrak{T} are given. We may also put as an approximation

$$\pi_\alpha = \mathfrak{P} e^{b \left(1 - \frac{T_\alpha}{T}\right)}$$

$$\pi_\beta = \mathfrak{P} e^{b \left(1 - \frac{T_\beta}{T}\right)}$$

where T_α and T_β are the temperatures at which the vapour pressures of \mathfrak{S}_α and \mathfrak{S}_β are equal to \mathfrak{P} . The value of b depends on the chosen value of \mathfrak{P} as we have seen in the preceding chapter.

Now it is possible to determine the constants Ω , \mathfrak{T} , T_α , and T_β by means of equation (5), when the specific volumes and the pressures of the saturated vapours at two different temperatures are given, provided we can hit upon the proper value of ν . This can certainly be done after a few trials. In this case we have the following sets of equations

$$\left. \begin{aligned} C'_{\alpha 1} P_1 &= C_{\alpha 1} \mathfrak{P} e^{b \left(1 - \frac{T_\alpha}{T_1}\right)} \\ (1 - C'_{\alpha 1}) P_1 &= (1 - C_{\alpha 1}) \mathfrak{P} e^{b \left(1 - \frac{T_\beta}{T_1}\right)} \end{aligned} \right\}$$

$$\left. \begin{aligned} C'_{\alpha 2} P_2 &= C_{\alpha 2} \mathfrak{P} e^{b \left(1 - \frac{T_\alpha}{T_2}\right)} \\ (1 - C'_{\alpha 2}) P_2 &= (1 - C_{\alpha 2}) \mathfrak{P} e^{b \left(1 - \frac{T_\beta}{T_2}\right)} \end{aligned} \right\}$$

where C_α is the molar fraction of \mathfrak{S}_α in the gas phase, and the suffixes denote the relation to the chosen temperatures T_1 and T_2 . C_α can be calculated from the specific volume of the vapour. If we make $\mathfrak{P} =$ one atmosphere, the value of b is known, and T_α and T_β are the respective boiling points. By equation (27) we can express $C_{\alpha 1}$ and $C_{\alpha 2}$ in terms of \mathfrak{Q} and \mathfrak{T} . There being thus four equations to evaluate four unknown constants, the problem can be solved, and the correctness of the values so obtained can be tested by means of the vapour pressures at other temperatures. In this way it will be possible to determine the degree of association of liquids with tolerable accuracy. But the calculation will be somewhat tedious.

It has been frequently observed that the vapour is not polymerised to any noticeable degree, while the liquid must be looked upon as highly associated. In such cases π_β is very small in comparison with π_α , and equation (27) is reduced to

$$P = C_\alpha \pi_\beta \dots\dots\dots (29)$$

In order to evaluate \mathfrak{Q} , \mathfrak{T} , and T_α in such cases the vapour pressures at three different temperatures must be given besides the value of ν .

Differentiating both sides of equation (29) with respect to T , we get

$$\frac{\partial P}{\partial T} = C_\alpha \frac{\partial \pi_\alpha}{\partial T} + \pi_\alpha \frac{\partial C_\alpha}{\partial T} = \left(\frac{1 - C_\alpha}{\nu - (\nu - 1) C_\alpha} \mathfrak{Q} + q_\alpha \right) \frac{P}{RT^2},$$

where $\frac{1 - C_\alpha}{\nu - (\nu - 1) C_\alpha} \mathfrak{Q} + q_\alpha$ is the quantity of heat absorbed during the production of one mol of the vapour. Now if TROUTON'S law be valid for all normal liquids under all pressures below a certain value, as indicated in the foregoing chapter, DÜHRING'S

relation must hold, and the temperatures at which the liquids have an equal vapour pressure must be proportional to the absolute temperature of the boiling points. This has been found to be the case approximately for a great many unassociated liquids. Hence the vapour pressure curves of these liquids do not intersect one another, at least at pressures below 1000 m.m. of mercury. On the other hand the vapour pressure curves of associated liquids mostly intersect those of the normal liquids, and indeed they are at the points of intersection generally steeper than the normal curves. If the heat of evaporation of a normal liquid under the pressure P be q , then in most cases

$$q_{\alpha} + \frac{1 - C_{\alpha}}{\nu - (\nu - 1) C_{\alpha}} \mathfrak{D} > q.$$

But as a consequence of TROUTON'S law

$$q_{\alpha} < q.$$

Hence in many cases $\frac{1 - C_{\alpha}}{\nu - (\nu - 1) C_{\alpha}} \mathfrak{D}$ must have considerable value.

In other words, the heat of dissociation must be considerable.

As an illustration of what has been said in the foregoing paragraphs we may adduce the vapour tension of acetone. As will be shown in § 2 (b) it is possible to determine the value of ν and \mathfrak{R} from the vapour pressure of binary mixtures which consist of a normal liquid and the associated liquid under consideration. From the data of CUNAEUS at 0°C, it has been concluded that $\nu = 3$ and $\pi_{\alpha} = 162$ m.m. As the vapour density of acetone is normal π_{β} must be very small, so that equation (29) may be applied. The vapour pressure of acetone at 0° is $P = 69.6$ m.m. from which we get $\mathfrak{R} = 0.1495$. The hypothetical vapour pressure of pure simple acetone at various temperatures can be represented by

$$\pi_{\alpha} = e^{10.9 \left(1 - \frac{311.71}{T}\right)}$$

where the unit of pressure is one atmosphere and 311.71 is the hypothetical absolute boiling point. 10.9 is the general constant according to the law of TROUTON and the constant 311.71 is determined from the data at 0°. Now if a second point on the vapour pressure curve be given, Δ and \mathfrak{T} can be determined. ZAWIDZKI found the vapour pressure of acetone at 35.17° to be 344.2, from which we get

$$\Delta = 3290 \text{ calories}$$

$$\mathfrak{T} = 404.43.$$

With these constants the vapour pressure of acetone at various temperatures has been calculated as shown in the following table.

TABLE 1.¹⁾

t	C_{α}	ξ	P (calculated)	P (observed)
0°	0.4296	2.1408	69.6 m.m.	(69.6 m.m.)
5°	0.4422	2.1156	89.6 "	—
10°	0.4546	2.0908	114.4 "	—
15°	0.4668	2.0664	144.6 "	—
20°	0.4787	2.0426	181.4 "	182.5 "
25°	0.4904	2.0192	225.7 "	229. "
30°	0.5018	1.9964	278.8 "	281. "
35°	0.5130	1.9740	341.9 "	343. "
35.17°	0.5132	1.9736	344.2 "	(344.2 ")
40°	0.5239	1.9522	416.5 "	416. "
45°	0.5346	1.9308	504.1 "	505. "
50°	0.5450	1.9100	606.3 "	607. "
55°	0.5552	1.8896	725.1 "	721. "
60°	0.5652	1.8696	862.1 "	860. "

1) This table has been calculated by Y. YAMASAKI, a student of chemistry.

In the table the result of calculation is compared with the observation of A. E. TAYLOR (Journ. phys. Chem., 4, 336; 1900). The agreement is quite satisfactory. The degree of association ξ has been calculated by equation (26).

The heat of evaporation for one mol of vapour at the boiling point 56.2° has been calculated to be

$$\frac{1-C_\alpha}{\xi} \Delta + q_\alpha = 7520 \text{ calories.}$$

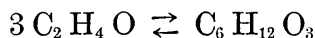
[q_α is set $10.9 \times 311.71 \times 1.985 = 6744$ calories]. The calculation according to the well known equation,

$$\text{Molecular heat of evaporation} = \frac{R (\ln P_1 - \ln P_2)}{\frac{1}{T_2} - \frac{1}{T_1}},$$

from TAYLOR's data gives 7640 calories, while WIRTZ (Landolt-Börnstein-Meyerhofer's Tabellen) has determined it to 7300 calories. Were acetone a normal liquid the molecular heat of evaporation would amount to only 6960 calories.

(c) *Acetaldehyde and Paraldehyde.*

The equilibrium between acetaldehyde and paraldehyde has been studied by HOLLMANN (Zeits. physik. Chem., 43, 129; 1903) under the guidance of ROOZEBOOM. The peculiarity of the system is that the reaction



proceeds so very slowly at lower temperatures, that the chemical species can be treated as independent components, while at higher temperatures or in the presence of catalysers the reaction takes place so rapidly that the state of equilibrium is reached in a

very short time. From HOLLMANN's data we may conclude that the mixture of the two chemical species behaves approximately as an ideal solution, the fusion curve having nearly the form represented by equation (17)

$$\ln C_1 = \frac{Q}{R} \left(\frac{1}{T_1} - \frac{1}{T} \right),$$

as is to be seen from the following table.

TABLE 2.

Fusion curve of the system paraldehyde and acetaldehyde.

$T-273$	C_β	C_β (calculated)	Q
12.55°	1.000	1.000	—
8.90°	0.928	0.921	3279
6.60°	0.879	0.874	3441
3.70°	0.821	0.816	3502
0.93°	0.767	0.764	3549
-1.02°	0.727	0.726	3585
-4.00°	0.676	0.677	3612
-6.65°	0.633	0.633	3600
-9.10°	0.584	0.594	3722
-11.1°	0.545	0.564	3818
-12.2°	0.525	0.548	3855
-13.0°	0.513	0.536	3855
-14.1°	0.493	0.521	3900
-16.4°	0.460	0.489	3907
-17.7°	0.444	0.463	3798
-23.0°	0.381	0.406	3852
-26.5°	0.345	0.366	3814
-29.8°	0.313	0.331	3786
-33.0°	0.284	0.299	3759
-33.7°	0.279	0.294	3749

-38.0°	0.245	0.256	3712
-42.6°	0.217	0.219	3623
-46.8°	0.192	0.189	3570
-52.5°	0.167	0.154	3444
-58.2°	0.144	0.124	3340
-62.0°	0.130	0.106	3277
-65.8°	0.117	0.091	3221
-68.0°	0.109	0.083	3201
-68.5°	0.106	0.081	3214
-71.5°	0.098	0.071	3162
-77.5°	0.086	0.054	3023
-91.76°	0.044	0.026	3081
-113.51°	0.033	0.007	3085
-119.18°	0.016	0.004	2742

C_β is the molar fraction of paraldehyde. Q , the molecular heat of fusion of this substance, has been calculated from the fusion points by equation (17). The values of Q for lower temperatures are not reliable, because the composition of the solution must have suffered considerable change on account of the separation of the paraldehyde as the solid phase; and this source of error is the more considerable as the molar fraction of paraldehyde is the smaller. The notable decrease in the value of Q for $C_\beta < 0.2$ is doubtless due to this cause. On the whole it appears as if Q increases with a lowering temperature. If we assume

$$Q = 3600 \text{ calories}$$

and recalculate the molar fraction C_β for observed fusion points, the agreement with experimental data is tolerably good, the maximum difference being less than 0.03.

HOLLMANN has also measured the boiling points of various mixtures of the two chemical species. The following calculation

is based on the data given in his second table. The temperatures have been corrected for a pressure of 760 m.m. This could be done without difficulty because the differences do not exceed 6 m.m. The compositions of the mixtures corresponding to the boiling points have been calculated by means of equation (11)

$$C_{\beta} e^{b\left(1-\frac{T_{\beta}}{T}\right)} + (1-C_{\beta}) e^{b\left(1-\frac{T_{\alpha}}{T}\right)} = 1,$$

where C_{β} is the molar fraction of paraldehyde as before, and T_{α} and T_{β} are the boiling points of the two chemical species. For b the approximate value, 11, has been used. In the following table the results of calculation are compared with observed values.

TABLE 3.

The boiling points of the system paraldehyde and acetaldehyde.

$T-273$	C_{β}	C_{β} (calculated)
21.0°	0	0
27.1°	0.201	0.205
32.7°	0.349	0.353
39.8°	0.501	0.497
40.8°	0.523	0.514
43.1°	0.561	0.551
56.9°	0.703	0.721
72.7°	0.798	0.838
103.0°	0.916	0.963
123.9°	1.000	1.000

Up to the molar fraction 0.7 the agreement between the values observed and calculated is tolerably good. That the differences for larger values of C_{β} are so great is doubtless due to the fact that a comparatively large amount of acetaldehyde

was volatilized and was present partly in the gaseous phase and partly in the reverse condenser as liquid. This source of error must be the more serious, the greater the molar fraction of paraldehyde. It is therefore to be regretted that the author determined the composition of the solution from the quantities of the substances put into the boiling vessel and not in a manner more direct. Moreover the boiling point of paraldehyde is more than a hundred degrees higher than that of the other component, a difference certainly too large for the exact applicability of equation (11).

It is not improbable that the chemical species of an associated liquid as a rule behave towards each other as the components of ideal solutions.

According to HOLLMANN the freezing point of the system acetaldehyde \rightleftharpoons paraldehyde in the presence of a catalyser lies at

$$T-273^{\circ} = 6.75^{\circ}$$

This temperature he calls the natural freezing point of the system, and corresponds to the freezing point of an associated liquids as it is usually observed. The composition of the system at this point is

$$C_{\beta} = 0.883.$$

The natural boiling point of the system has been determined to be

$$T-273^{\circ} = 41.6^{\circ},$$

with the composition

$$C_{\beta} = 0.534.$$

From these two sets of values we obtain for the constants of equation (27)

$$\mathfrak{Z} = 329.4$$

$$\mathfrak{Q} = 23340 \text{ calories.}$$

The heat of polymerisation \mathfrak{Q} can also be calculated from the thermochemical data. BERTHELOT and DELEPINE found the heat of combustion of acetaldehyde $\text{C}_2\text{H}_4\text{O}$ to be 279150 calories, while the heat of combustion of paraldehyde $\text{C}_6\text{H}_{12}\text{O}_3$ amounts to 813200 calories according to LOUGUININE. Hence

$$\mathfrak{Q} = (3 \times 279150 - 813200) \text{ cal.} = 24250 \text{ cal.}$$

The agreement must be looked upon as quite satisfactory, when we take the errors of thermochemical measurements into consideration.

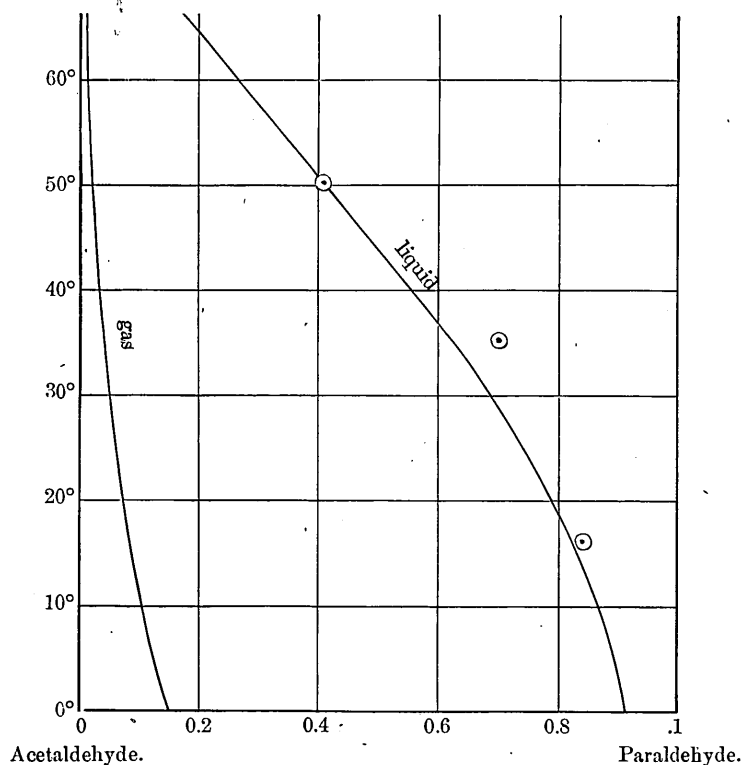


Fig. 11.

For the calculation of the natural vapour pressure curve of the system according to equation (28) we have the following relations :

$$\frac{(1-C_\beta)^3}{C_\beta} = \mathfrak{K} = e^{\frac{23340}{1.985} \left(\frac{1}{329.4} - \frac{1}{T} \right)}$$

$$\pi_\alpha = e^{11 \left(1 - \frac{294}{T} \right)}$$

$$\pi_\beta = e^{11 \left(1 - \frac{396.9}{T} \right)}$$

where the unit of pressure is one atmosphere. The results of the calculation are given in the following table.

TABLE 4.

The natural vapour tension curve of the system
acetaldehyde \rightleftharpoons paraldehyde.

$T-273^\circ$	\mathfrak{K}	C_β	C_β'	π_α	π_β	P
0°	0.000635	0.9165	0.1483	0.429	0.00679	0.0421
10°	0.00289	0.8642	0.1044	0.652	0.01195	0.0989
20°	0.01197	0.789	0.0727	0.963	0.02024	0.2192
30°	0.0445	0.687	0.0496	1.386	0.03310	0.4565
40°	0.1546	0.558	0.0359	1.949	0.05242	0.8150
50°	0.4943	0.412	0.0203	2.684	0.08074	1.611
60°	1.473	0.267	0.0121	3.626	0.1211	2.690

TURBABA found at 50.5° $C_\beta = 0.405$ and $P = 1.5-2$, while the calculation gives $C_\beta = 0.394$ and $P = 1.65$.

The temperature-composition diagram shown in Fig. 11 is constructed from the preceding table. The data found by TURBABA are marked with circlets. These are but rough estimations with the exception of the datum for 50.5° which, being the mean of a large number of tolerably concordant determinations, must be considered accurate.

(d) *Physical Properties of Associated Liquids.*

The classical researches of KOPP and LANDOLT have called forth a great many investigations on the relations existing between physical properties and chemical composition, particularly of liquids. But the work in this field slackened after a time, partly owing to the rapid development of physical chemistry which put forth so many interesting problems for solution, and partly owing to the fact that the regularities found were mostly imperfect and could not be brought into well defined simple schemes. This is no doubt to a great extent due to the fact that the investigators did not distinguish between normal and associated liquids. It is self-evident that no good result can be obtained when, for example, the system acetaldehyde \rightleftharpoons paraldehyde is treated as if it consisted of acetaldehyde alone. Such irrational procedure has hitherto been quite general. But if the molecular formulæ and the relative amounts of the chemical species constituting associated liquids be determined by any reliable method, then we shall be in a position to estimate the physical properties of individual species. The comparison of various chemical species will then no doubt show greater regularities.

§ 2. **Quasi-ideal Solutions with a Normal and an Associated Component.**

(a) *Homogeneous Equilibrium.*

In the present case we have

$$C_{\alpha} + C_{\beta} + C = 1, \dots\dots\dots(30)$$

when we assume as in the foregoing section the associated component to consist of two chemical species \mathfrak{S}_α and \mathfrak{S}_β , and express the molar fraction of the normal component \mathfrak{S} by C . But these molar fractions are mostly unknown. The molar fractions usually given are calculated on the supposition that the associated component consists of the simpler chemical species \mathfrak{S}_α alone. These we propose to call *empirical* molar fractions. Now let x be the empirical molar fraction of the associated component, then $1-x$ is the empirical molar fraction of the normal substance. The relation between these two sorts of molar fractions is expressed by the following equation :

$$x = \frac{C_\alpha + \nu C_\beta}{C_\alpha + \nu C_\beta + C} = \frac{C_\alpha + \nu C_\beta}{1 + (\nu - 1) C_\beta} \dots\dots\dots(31)$$

As the solution is supposed to be quasi-ideal, equation (25) must hold, which may be written

$$\frac{C_\alpha^\nu}{C_\beta} = \mathfrak{K} = e^{\frac{\mathfrak{Q}}{R} \left(\frac{1}{\mathfrak{T}} - \frac{1}{T} \right)} \dots\dots\dots(32)$$

At a constant temperature \mathfrak{K} is constant and we have

$$x = \frac{C_\alpha + \nu \frac{C_\alpha^\nu}{\mathfrak{K}}}{1 + (\nu - 1) \frac{C_\alpha^\nu}{\mathfrak{K}}} \dots\dots\dots(33)$$

or

$$x = \frac{\frac{1}{\mathfrak{K}^\nu} C_\beta^\nu + \nu C_\beta}{1 + (\nu - 1) C_\beta}, \dots\dots\dots(34)$$

while for the molar fraction of the normal component we get from equations (30) and (31)

$$C = \{1 + (\nu - 1) C_\beta\} (1 - x). \dots\dots\dots(35)$$

These relations may be made more conspicuous by means

of graphical representations in which x is taken as the abscissa and the molare fractions as the ordinate. From equation (33) we get by differentiation

$$\begin{aligned}\frac{dC_\alpha}{dx} &= \frac{\left(1 + \frac{\nu-1}{\mathfrak{K}} C_\alpha^\nu\right)^2}{1 - \frac{(\nu-1)^2}{\mathfrak{K}} C_\alpha^\nu + \frac{\nu^2}{\mathfrak{K}} C_\alpha^{\nu-1}} = \frac{\{1 + (\nu-1) C_\beta\}^2}{1 - (\nu-1)^2 C_\beta + \frac{\nu^2 C_\beta}{C_\alpha}} \dots (36) \\ \frac{d^2 C_\alpha}{dx^2} &= \frac{\left\{(\nu+1)C_\alpha - \frac{(\nu-1)^2}{\mathfrak{K}} C_\alpha^{\nu+1} + \frac{\nu(\nu-1)}{\mathfrak{K}} C_\alpha^\nu\right\} \frac{\nu(\nu-1)}{\mathfrak{K}} C_\alpha^{\nu-1} \left(1 + \frac{\nu-1}{\mathfrak{K}} C_\alpha^\nu\right)^3}{\left\{1 - \frac{(\nu-1)^2}{\mathfrak{K}} C_\alpha^\nu + \frac{\nu^2}{\mathfrak{K}} C_\alpha^{\nu-1}\right\}^3} \\ &= \left[(\nu+1)C_\alpha + \nu(\nu+1)C_\beta - (\nu-1)^2 C_\alpha C_\beta - \nu \right] \frac{\nu(\nu-1)}{\mathfrak{K}} C_\alpha^{\nu-1} \left\{ \frac{1 + \frac{\nu-1}{\mathfrak{K}} C_\alpha^\nu}{1 - \frac{(\nu-1)^2}{\mathfrak{K}} C_\alpha^\nu + \frac{\nu^2}{\mathfrak{K}} C_\alpha^{\nu-1}} \right\}^3\end{aligned}$$

because $\frac{C_\alpha^\nu}{\mathfrak{K}} = C_\beta$ by equation (32).

$\frac{dC_\alpha}{dx}$ is positive for all values of x because C_α is less than unity. At $x = 0$ we have

$$\left(\frac{dC_\alpha}{dx}\right)_0 = 1 \dots\dots\dots (37)$$

because C_β vanishes as x approaches zero, while at $x = 1$ $C_\alpha + C_\beta = 1$ and the differential coefficient becomes

$$\left(\frac{dC_\alpha}{dx}\right)_1 = (C_\alpha)_1, \dots\dots\dots (38)$$

where $(C_\alpha)_1$ denotes the molar fraction of \mathfrak{S}_α in the associated component in the pure state.

The sign of the second differential coefficient $\frac{d^2 C_\alpha}{dx^2}$ is determined by that of the factors in the rectangular brackets, because the other factors are necessarily positive. For small values of x

both C_α and C_β are small and $\frac{d^2C_\alpha}{dx^2}$ is negative. But for large values of x it becomes positive, and at $x = 1$ we have

$$\left(\frac{d^2C_\alpha}{dx^2}\right)_1 = (\nu C_\beta + C_\alpha)^2$$

which is of course positive.

Hence, when we represent the relation between C_α and x in a diagram, we get a curve like α in Fig. 12. The curve has for its tangent at $x = 0$ the diagonal OA which lies completely above it. The curve is concave towards the axis of x for small values of x , and turns

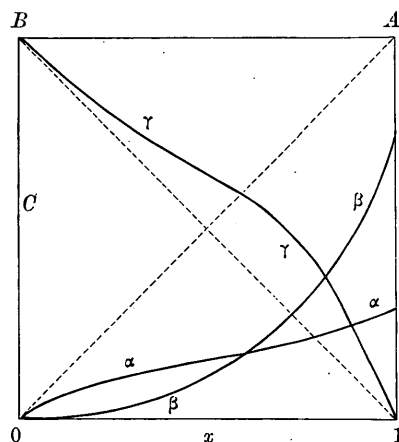


Fig. 12.

convex as x approaches unity. The tangent at $x = 1$ is a straight line which passes through the origin 0.

From equation (34) we get by differentiation

$$\begin{aligned} \frac{dC_\beta}{dx} &= \frac{\{1 + (\nu - 1) C_\beta\}^2}{\nu + \frac{1}{\nu} \Re^{\frac{1}{\nu}} C_\beta^{\frac{1}{\nu} - 1} - \frac{(\nu - 1)^2}{\nu} \Re^{\frac{1}{\nu}} C_\beta^{\frac{1}{\nu}}} \\ &= \frac{\{1 + (\nu - 1) C_\beta\}^2}{\nu + \frac{1}{\nu} \frac{C_\alpha}{C_\beta} - \frac{(\nu - 1)^2}{\nu} C_\alpha} \dots\dots\dots (39) \end{aligned}$$

and

$$\begin{aligned} \frac{d^2C_\beta}{dx^2} &= (\nu - 1) \left\{ 2 \nu + \frac{1}{\nu^2} \Re^{\frac{1}{\nu}} C_\beta^{\frac{1}{\nu} - 2} + \frac{2}{\nu^2} \Re^{\frac{1}{\nu}} C_\beta^{\frac{1}{\nu} - 1} \right. \\ &\quad \left. - \left(\frac{\nu - 1}{\nu} \right)^2 (2 \nu - 1) \Re^{\frac{1}{\nu}} C_\beta^{\frac{1}{\nu}} \right\} \left\{ \frac{1 + (\nu - 1) C_\beta}{\nu + \frac{1}{\nu} \frac{C_\alpha}{C_\beta} - \frac{(\nu - 1)^2}{\nu} C_\alpha} \right\}^3 \end{aligned}$$

or as $\mathfrak{R}^{\frac{1}{\nu}} C_{\beta}^{\frac{1}{\nu}} = C_{\alpha}$ from equation (32)

$$\frac{d^2 C_{\beta}}{dx^2} = (\nu - 1) \left\{ 2\nu + \frac{1}{\nu^2} \frac{C_{\alpha}}{C_{\beta}^2} + \frac{2}{\nu^2} \frac{C_{\alpha}}{C_{\beta}} - \left(\frac{\nu - 1}{\nu} \right)^2 (2\nu - 1) C_{\alpha} \right\} \left\{ \frac{1 + (\nu - 1) C_{\beta}}{\nu + \frac{1}{\nu} \frac{C_{\alpha}}{C_{\beta}} - \frac{(\nu - 1)^2}{\nu} C_{\alpha}} \right\}^2$$

As both C_{α} and C_{β} are necessarily less than unity, $\frac{dC_{\beta}}{dx}$ as well as $\frac{d^2 C_{\beta}}{dx^2}$ must be positive throughout. We see further from equation (32) that C_{β} approaches zero far more rapidly than C_{α} when x approaches zero. Hence at $x = 0$

$$\left(\frac{dC_{\beta}}{dx} \right)_0 = 0 \quad \dots\dots\dots(40)$$

and $\frac{d^2 C_{\beta}}{dx^2}$ is also zero. On the other hand at $x = 1$ we have

$$\left(\frac{dC_{\beta}}{dx} \right)_1 = \nu (C_{\beta})_1 \quad \dots\dots\dots(41)$$

where $(C_{\beta})_1$ denotes the molar fraction of \mathfrak{S}_{β} in the associated component in the pure state. From these considerations it is clear that the curve showing the relation between x and C_{β} must have a form like β in Fig. 12.

As to the curve representing the molar fraction of the normal component as a function of x , we see from equation (35) that it must throughout lie above the diagonal $B1$ (Fig. 12). Its shape can be further elucidated from the following considerations. From equation (30) we have

$$\frac{dC}{dx} = - \frac{dC_{\alpha}}{dx} - \frac{dC_{\beta}}{dx},$$

and as both $\frac{dC_\alpha}{dx}$ and $\frac{dC_\beta}{dx}$ are positive, $\frac{dC}{dx}$ must be negative throughout. Hence C decreases continuously with increasing values of x . At $x = 0$ C is equal to unity, while at $x = 1$ it is reduced to zero. Again in the equation

$$\frac{d^2C}{dx^2} = -\frac{d^2C_\alpha}{dx^2} - \frac{d^2C_\beta}{dx^2}$$

$\frac{d^2C_\alpha}{dx^2}$ is negative for smaller values of x , while $\frac{d^2C_\beta}{dx^2}$, though positive, is very small. Hence $\frac{d^2C}{dx^2}$ must be positive for small values of x and the curve is convex towards the axis of x . With increasing values of x $\frac{d^2C_\alpha}{dx^2}$ becomes positive too, while $\frac{d^2C_\beta}{dx^2}$ remains positive and increases in amount, so that $\frac{d^2C}{dx^2}$ must turn negative at a certain value of x and from this point the curve becomes concave. The form of the curve must therefore be like that of γ in Fig. 12.

Again from equation (35) we have by differentiation

$$\frac{dC}{dx} = (\nu-1)(1-x) \frac{dC_\beta}{dx} - \{1 + (\nu-1) C_\beta\}.$$

Hence at $x = 0$,

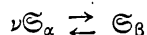
$$\left(\frac{dC}{dx}\right) = -1, \dots\dots\dots(42)$$

that is to say the tangent to the curve at $x = 0$ is the diagonal $B1$. At $x = 1$ we have

$$\left(\frac{dC}{dx}\right)_1 = -\{1 + (\nu-1) C_\beta\}, \dots\dots\dots(43)$$

which says that the tangent at $x = 1$ is equal to the degree of association of the pure associated component taken negative.

Thus we see that the state of homogeneous equilibrium at a constant temperature in a system consisting of an associated and a normal component and in which the reversible reaction



takes place, can be completely represented by a diagram like that shown in Fig. 12.

(b) *The Equilibrium between a Gaseous and a Liquid Phase.*

(1) *Vapour Pressure at a Constant Temperature.*

Let p_α , p_β , and p be the partial pressures of \mathfrak{S}_α , \mathfrak{S}_β , and \mathfrak{S} respectively in the gas phase which is in equilibrium with the solution consisting of these chemical species, and let P be the vapour tension of the pure \mathfrak{S} . Then we have by equation (5)

$$p_\alpha = C_\alpha \pi_\alpha,$$

$$p_\beta = C_\beta \pi_\beta,$$

$$p = C P_0,$$

and

$$P = C_\alpha \pi_\alpha + C_\beta \pi_\beta + C P_0, \dots \dots \dots (44)$$

where P is the total pressure.

The curves representing the relation between these partial pressures and the empirical molar fractions must have forms resembling those given in Fig. 12. As a rule π_α will be far larger than π_β , so that the curve for p_β will often lie far below that for p_α .

When these curves of partial pressures are given, we can

evaluate the characteristic magnitudes of the system such as π_α , π_β , and \mathfrak{R} . According to equations (5) and (37) π_α can be found by producing the tangent at $x = 0$ to the curve of p_α so as to meet the pressure axis at $x = 1$. The height of the point of intersection is equal to π_α .

From the value of p_α at $x = 1$ the molar fraction of \mathfrak{S}_α in the pure associated component can be determined, and then π_β can be calculated from p_β at $x = 1$.

ν can also be determined from the tangent of the angle, which the curve of p makes with the x axis at $x = 1$. From equation (5) and (43) we have

$$\left(\frac{dp}{dx}\right)_1 = P_0 \left(\frac{dC}{dx}\right)_1 = -\{1 + (\nu - 1)(C_\beta)_1\} P_0$$

Hence ξ , the degree of association of the pure associated component, is given by

$$\xi = 1 + (\nu - 1)(C_\beta)_1 = -\frac{\left(\frac{dp}{dx}\right)_1}{P_0};$$

and for ν we have

$$\nu = \frac{-\frac{\left(\frac{dp}{dx}\right)_1}{P_0} - 1}{(C_\beta)_1} + 1 \dots\dots\dots(45)$$

When ν is thus determined \mathfrak{R} can be calculated from equation (32), and we are now in a position to give a quantitative account not only of the vapour pressures, total and partial, of the whole system, but also of the state of chemical equilibrium in the homogeneous solution, liquid as well as gaseous.

As the measurement of the partial pressures, or molar fractions in the gas phase, is rather troublesome, it often happens that the curve of the total pressure alone is determined. Even

in such cases the characteristic magnitudes can be evaluated in the following manner, provided the measurement of pressure and composition at both ends of the curve is sufficiently accurate.

The tangent to the total pressure curve may be expressed as follows:

$$\frac{dP}{dx} = \pi_{\alpha} \frac{dC_{\alpha}}{dx} + \pi_{\beta} \frac{dC_{\beta}}{dx} + P_0 \frac{dC}{dx}.$$

At the end where $x = 0$ equations (37), (40), and (42) hold. Hence

$$\left(\frac{dP}{dx} \right)_0 = \pi_{\alpha} - P_0$$

and we get

$$\pi_{\alpha} = \left(\frac{dP}{dx} \right)_0 + P_0 \dots\dots\dots(46)$$

In other words the tangent to the total pressure curve at $x = 0$ intersects the pressure axis at $x = 1$ at the height of π_{α} .

At the other end of the curve we have

$$(P)_1 = \pi_{\alpha} (C_{\alpha})_1 + \pi_{\beta} \{1 - (C_{\alpha})_1\} \dots\dots\dots(47)$$

These two equations, (46) and (47), do not suffice for the determination of the three quantities ν , $(C_{\alpha})_1$ and π_{β} . Another experimental datum is necessary for the purpose. The density of the saturated vapour of the pure associated component at the given temperature may be measured and employed to evaluate $(C_{\alpha})_1$. Or a point in the middle portion of the total pressure curve may be taken into calculation; then a few trials will suffice to determine the value of ν .

It has been frequently observed that the vapours of associated liquids have normal densities, that is densities corresponding to the molecular weight of the simple chemical species

\mathfrak{S}_α . In such cases π_β must be so small that p_β remains negligible in comparison with other pressures. Then we have

$$(C_\alpha)_1 = \frac{(P)_1}{\pi_\alpha} \dots\dots\dots(48)$$

and

$$\nu = \frac{\frac{(P)_1 - \left(\frac{dP}{dx}\right)_1}{P_0} - 1}{1 - (C_\alpha)_1} + 1. \dots\dots\dots(49)$$

When π_α and π_β are known for one temperature then they are known at least approximately for the range of 30° to 50° above and below that temperature. I mean that it is possible to evaluate T_α and T_β in the equations

$$\pi_\alpha = e^{b\left(1 - \frac{T_\alpha}{T}\right)}$$

$$\pi_\beta = e^{b\left(1 - \frac{T_\beta}{T}\right)}$$

because b has approximately the value of 10.9 for all chemical species, when the pressure is given in atmospheres, as shown in § 2 (c), of the preceding chapter.

The quantities \mathfrak{D} and \mathfrak{T} , which determine \mathfrak{K} as a function of temperature can be evaluated when the tension and density of the saturated vapour of the pure associated component are given for another temperature. In the cases where the vapours have normal densities, only the knowledge of the vapour tension is required.

When the four characteristic quantities \mathfrak{D} , \mathfrak{T} , T_α and T_β are known, the state of chemical equilibrium in the system composed of the associated compound alone or with other normal

components, can be described quantitatively for varying temperatures and pressures. We thus see the important service which the study of the vapour tension may render to the solution of chemical problems. In the following is given a concrete example in which the foregoing deductions are completely realised.

(2) *The System Acetone and Ethyl Oxide.*

The total and partial pressures of this system at 0°C. have been studied by CUNAEUS (*Zeits. physik. Chem.*, **36**, 232; 1901). Unfortunately I have not been able to consult the dissertation in which he has given a detailed account of the measurements. This is the more to be regretted because there seems to be several misprints in the numerical data given in the "*Zeitschrift*," as has been noticed by BAKHUIS ROOZEBOOM (*Heterogene Gleichgewichte*, II, 27, foot-note). In the following table his data are reproduced.

TABLE 5.¹⁾

x	x'		P in m.m.
0	0	0	185.6
0.165	(0.139)	0.12	181.2
0.383	(0.272)	0.22	166.8
0.490	(0.330)	0.27	158.0 (150.)
0.636	(0.383)	0.35	142.3
0.808	—	—	117.0
0.844	(0.554)	0.54	110.5 (118.5)
1.000	—	1.00	69.6

1) x in the original paper is the empirical molar fraction of ether, while here it stands for that of acetone.

x' in the brackets is the empirical molar fraction of acetone in the gas phase, determined by means of the index of refraction. Unfortunately the method is not an exact one for gaseous mixtures so readily condensible. The other values are those calculated by CUNAEUS by means of the following equation given by VAN DER WAALS:

$$\frac{1}{P} \frac{dP}{d(1-x)} = \frac{x-x'}{x'(1-x')}$$

As the equation is deduced thermodynamically (see *Continuität* etc., 2, 137) it must be applicable irrespective of the chemical complexity of the liquid phase. The values so calculated deserve therefore more confidence, and these will be employed in the following calculation.

Two of the data on the total pressure are doubtful. I mean those corresponding to $x = 0.490$ and $x = 0.844$. In the original paper the numbers in the brackets are given. When an xP curve is drawn with the other six data we get quite a regular curve; these two values, however, deviate very far from the curve. Hence they have been replaced by the numbers in the column. I believe I am not making too free with the data given, particularly in view of the remark of ROOZEBOOM.

As is well known, ethyl ether is a substance very nearly normal, while acetone has been demonstrated by RAMSAY and SHIELDS to be associated, though its vapour density corresponds to the simple formula C_3H_6O . Hence in the gas phase of the system there are only two chemical species C_3H_6O and $(C_2H_5)_2O$, while in the liquid phase there are at least three, i.e. C_3H_6O , $(C_3H_6O)_n$, and $(C_2H_5)_2O$. Under the supposition that there is only one polymer of acetone the mode of calculation developed above may be applied to this case.

On tracing the curve of partial pressure for acetone and drawing the tangent to the curve at $x = 0$, the following approximate value has been found, for the vapour pressure of pure C_3H_6O

$$\pi_\alpha = 160. \text{ m.m.}$$

The tangent of the angle which the curve of partial pressure of ether makes with the x axis has been found to be nearly

$$\left(\frac{dp}{dx}\right)_1 = -400.$$

The molar fraction of C_3H_6O in pure acetone is

$$(C_\alpha)_1 = \frac{69.6}{160} = 0.435$$

and in consequence that of $(C_3H_6O)_\nu$ amounts to

$$(C_\beta)_1 = 0.565$$

ν can now be determined by equation (45)

$$\nu = \frac{-\left(\frac{dp}{dx}\right)_1 - 1}{\frac{P_0}{(C_\beta)_1}} = \frac{\frac{400}{185.6} - 1}{0.565} + 1 = 3.04.$$

There is no doubt that $\nu = 3$.

With these data the value of \mathfrak{R} for 0°C . is determined to be

$$\mathfrak{R} = \frac{C_\alpha^\nu}{C_\beta} = \frac{0.435^3}{0.565} = 0.1456.$$

From the total pressure curve we get values but slightly different.

$$\pi_\alpha = 162 \quad \text{and} \quad (C_\alpha)_1 = 0.430$$

and

$$\nu = \frac{(P)_1 - \left(\frac{dP}{dx}\right)_1 - 1}{\frac{P_0}{1 - (C_\alpha)_1} - 1} + 1 = \frac{69.6 - (-325) - 1}{\frac{185.6}{0.570} - 1} + 1 = 2.97.$$

We are now in a position to give the equations of the curves of the molar fractions of the three chemical species and of the total and partial pressures. These are

$$C_\beta = \left\{ \left[\frac{x}{6-4x} + \sqrt{\left(\frac{x}{6-4x} \right)^2 + \frac{0.1456}{(9-6x)^3}} \right]^{\frac{1}{3}} + \left[\frac{x}{6-4x} - \sqrt{\left(\frac{x}{6-4x} \right)^2 + \frac{0.1456}{(9-6x)^3}} \right]^{\frac{1}{3}} \right\}^3$$

$$C = (1 + 2 C_\beta)(1 - x)$$

$$C_\alpha = 1 - C_\beta - C$$

$$p_\alpha = 160. C_\alpha$$

$$p = 185.6 C$$

$$P = p_\alpha + p.$$

The curves calculated by means of these equations are reproduced in Figs. 13 and 14. The data found by CUNAEUS are marked with circlets. The agreement must be considered to be satisfactory, in as much as we have employed as the basis of calculation only the vapour pressures of pure acetone and ether and the tangents of the partial pressure curves at the ends.

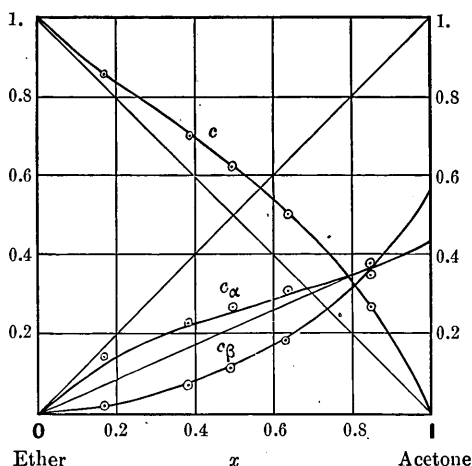


Fig. 13.

In order to make possible a more exact comparison the calculated values of molar fractions and pressures are given in the following tables together with the data obtained by CUNAEUS.

TABLE 6.

Molar fractions of the three chemical species.

x	C		C_α		C_β		x'	
	Direct	Calc.	Direct	Calc.	Direct	Calc.	Waals	Calc.
0	1.000	1.000	0	0	0	0	0	0
0.165	0.859	0.859	0.136	0.127	0.015	0.014	0.12	0.113
0.383	0.701	0.707	0.231	0.221	0.068	0.073	0.22	0.212
0.490	0.622	0.629	0.268	0.255	0.110	0.117	0.27	0.258
0.636	0.498	0.504	0.317	0.303	0.185	0.193	0.35	0.341
0.808	—	0.316	—	0.362	—	0.322	—	0.497
0.844	0.273	0.269	0.352	0.371	0.375	0.360	0.54	0.544
1.000	0	0	—	0.435	—	0.565	1.00	1.000

TABLE 7.

Total and partial pressures.

x	p		p_α		P	
	Cunaeus	Calc.	Cunaeus	Calc.	Found	Calc.
0	185.6	185.6	0	0	185.6	185.6
0.165	159.5	154.9	21.7	20.3	181.2	179.7
0.383	130.1	131.2	36.7	35.3	166.8	166.5
0.490	115.3	116.7	42.7	40.7	158.0	157.4
0.636	92.5	93.6	49.8	48.5	142.3	142.1
0.808	—	58.6	—	57.9	117.0	116.5
0.844	50.8	49.8	59.7	59.4	110.5	109.2
1.000	0	0	69.6	69.6	69.6	69.6

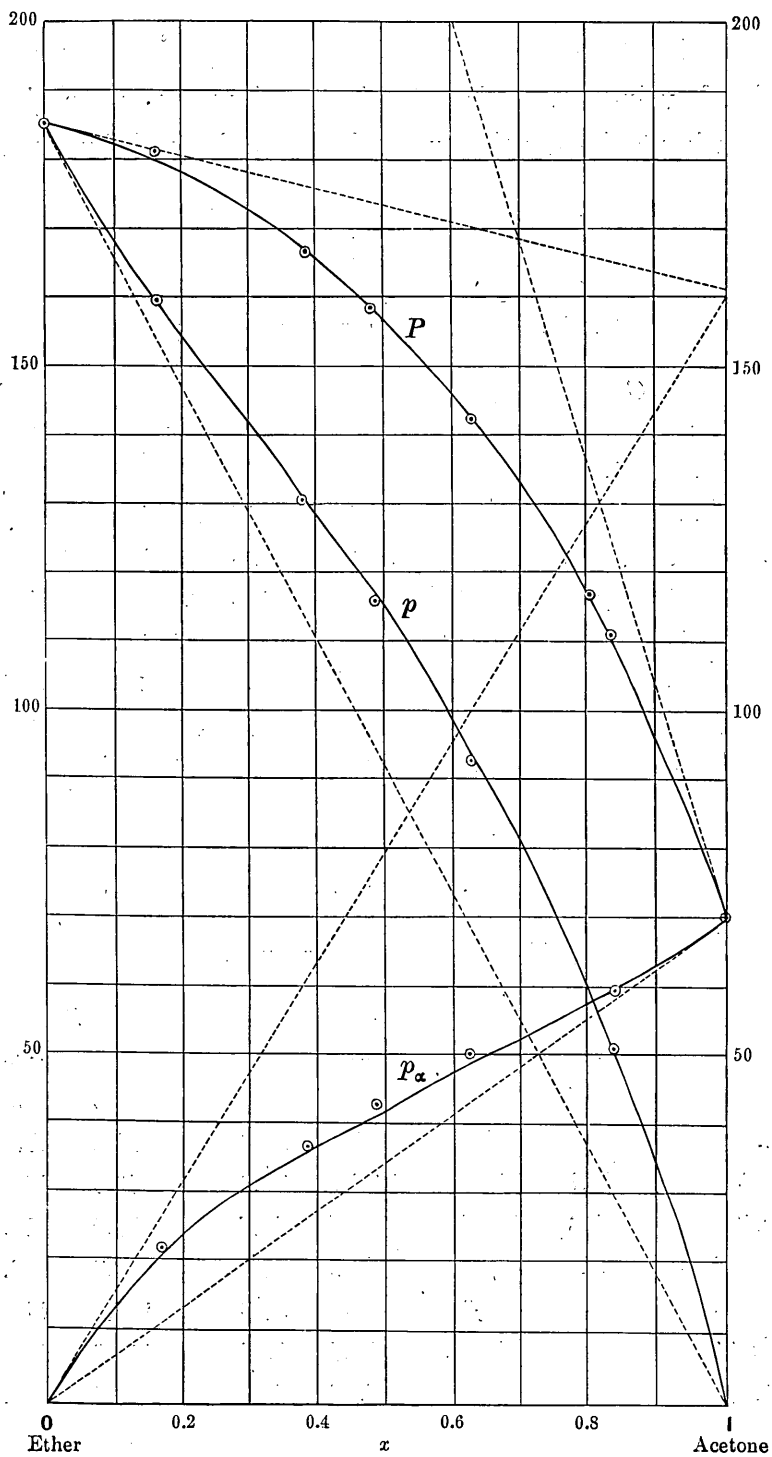


Fig. 14.

The molar fractions of the three chemical species under the heading "direct" have been calculated more directly from the data of CUNAEUS by means of the following equations,

$$C = \frac{(1-x')P}{185.6}$$

$$C_{\alpha} = \frac{x'P}{160}$$

$$C_{\beta} = 1 - C_{\alpha} - C.$$

The empirical molar fraction of the gas phase has been calculated as follows:

$$x' = \frac{p_{\alpha}}{p_{\alpha} + p}$$

the calculated partial pressures being employed.

It is quite probable that the other value for the vapour pressure of the pure chemical species C_3H_6O , that is $\pi_{\alpha} = 162$, is more in accordance with the facts. But the exact determination of tangents from curves being very difficult, better agreement could hardly be expected. At any rate the foregoing is quite enough to demonstrate that our theory is not a purely hypothetical construction which corresponds to no reality.

(3) *Boiling Point under Constant Pressure.*

Here we may proceed as in § 2 (c) of the preceding chapter. In equation (44)

$$C_{\alpha} \pi_{\alpha} + C_{\beta} \pi_{\beta} + C P_0 = P$$

we have now to consider P as constant, and the molar fractions as well as the vapour tensions of the pure chemical species as functions of temperature. C_{α} etc. can be expressed as explicit

functions of T and x by solving equations (33), (34), and (35), in which \mathfrak{R} is to be put, as in equation (32),

$$\mathfrak{R} = e^{\frac{\mathfrak{D}}{R} \left(\frac{1}{\mathfrak{T}} - \frac{1}{T} \right)}.$$

Now denote the given pressure by \mathfrak{P} , and remembering that

$$\frac{C_\alpha \pi_\alpha}{\mathfrak{P}} = C'_\alpha$$

$$\frac{C_\beta \pi_\beta}{\mathfrak{P}} = C'_\beta$$

$$\frac{C P_0}{\mathfrak{P}} = C'$$

where C'_α etc. are the molar fractions in the gas phase, and that

$$\pi_\alpha = \mathfrak{P} e^{b \left(1 - \frac{T'_\alpha}{T} \right)}$$

$$\pi_\beta = \mathfrak{P} e^{b \left(1 - \frac{T'_\beta}{T} \right)}$$

$$P_0 = \mathfrak{P} e^{b \left(1 - \frac{T'_\gamma}{T} \right)}$$

in which T'_α etc. are the boiling points of the pure chemical species under the given pressure, and b is a constant determined by the same, we have

$$\begin{aligned} \varphi_\alpha(x, T, \mathfrak{D}, \mathfrak{T}) e^{b \left(1 - \frac{T'_\alpha}{T} \right)} + \varphi_\beta(x, T, \mathfrak{D}, \mathfrak{T}) e^{b \left(1 - \frac{T'_\beta}{T} \right)} \\ + \varphi_\gamma(x, T, \mathfrak{D}, \mathfrak{T}) e^{b \left(1 - \frac{T'_\gamma}{T} \right)} = 1. \dots (50) \end{aligned}$$

for the equation representing the relation between the boiling point and the composition. This equation can indeed be employed for the calculation of the boiling point, but it is too complex for general discussion. Hence the study of the boiling point is not so well fitted for elucidating the chemical conditions of the

solution, as the study of vapour pressure at a constant temperature.

(c) *The Equilibrium between Liquid and Solid Phases.*

It has been shown by BECKMANN in his well known cryoscopic studies that the depression of the freezing point caused by associated substances such as alcohol in solutions in normal liquids, as for instance benzene, is sometimes far less than might be expected. This has been further confirmed by the investigations of various savants and particularly by those of AUWERS and his pupils. J. SCHROEDER (Zeits. physik. Chem., **11**, 449; 1893) has shown that the fusion curve of a normal substance deviates considerably from the ideal course, when the other component is associated, and indeed in the sense expected.

In the cases in which the conditions of quasi-ideal solutions are satisfied, the equations of the fusion curves can be readily obtained as shown in the sequel.

(1) *The Solid is the Normal Component.*

Since equation (7) must hold in this case, we have by (35)

$$C = \{1 + (\nu - 1) C_\beta\} (1 - x) = e^{\frac{Q}{R} \left(\frac{1}{T_0} - \frac{1}{T} \right)} \dots \dots \dots (51)$$

or

$$1 - x = \frac{e^{\frac{Q}{R} \left(\frac{1}{T_0} - \frac{1}{T} \right)}}{1 + (\nu - 1) C_\beta} \dots \dots \dots (52)$$

where T_0 is the melting point of the normal substance. Were both components normal,

$$1-x = e^{\frac{Q}{R} \left(\frac{1}{T_0} - \frac{1}{T} \right)};$$

hence the fusion point T for the equal values of x must be higher in the present case than in the ideal solution.

Since

$$C = 1 - C_\alpha - C_\beta = 1 - \Re^{\frac{1}{\nu}} C_\beta^{\frac{1}{\nu}} - C_\beta$$

we get from equation (51)

$$\Re^{\frac{1}{\nu}} C_\beta^{\frac{1}{\nu}} + C_\beta = 1 - e^{\frac{Q}{R} \left(\frac{1}{T_0} - \frac{1}{T} \right)}.$$

Solving this equation and substituting for \Re its equivalent in equation (32), we get C_β in terms of T , \mathfrak{D} , \mathfrak{T} , Q , and T_0 . Let this be

$$C_\beta = F(T, \mathfrak{T}, T_0, \mathfrak{D}, Q),$$

then

$$1-x = \frac{e^{\frac{Q}{R} \left(\frac{1}{T_0} - \frac{1}{T} \right)}}{1 + (\nu-1) F(T, \mathfrak{T}, T_0, \mathfrak{D}, Q)}.$$

For example, when $\nu = 3$

$$1-x = \frac{e^{\frac{Q}{R} \left(\frac{1}{T_0} - \frac{1}{T} \right)}}{1 + 2 \left\{ \sqrt[3]{\frac{1 - e^{\frac{Q}{R} \left(\frac{1}{T_0} - \frac{1}{T} \right)}}{2}} + \sqrt{\frac{\left\{ 1 - e^{\frac{Q}{R} \left(\frac{1}{T_0} - \frac{1}{T} \right)} \right\}^2}{4} + \frac{e^{\frac{Q}{R} \left(\frac{1}{T_0} - \frac{1}{T} \right)}}{27}} \right. \\ \left. + \sqrt[3]{\frac{1 - e^{\frac{Q}{R} \left(\frac{1}{T_0} - \frac{1}{T} \right)}}{2}} + \sqrt{\frac{\left\{ 1 - e^{\frac{Q}{R} \left(\frac{1}{T_0} - \frac{1}{T} \right)} \right\}^2}{4} + \frac{e^{\frac{Q}{R} \left(\frac{1}{T_0} - \frac{1}{T} \right)}}{27}} \right\}}$$

This equation has been tested by YAMAMOTO,¹⁾ and has been found to represent the fusion curve of naphthalene in the system naphthalene and phenol with a very close approximation.

1) See Art. 11 of this volume, where x denotes the empirical molar fraction of naphthalene and not that of phenol, as is implied in the foregoing deductions.

The fusion point of the normal substance can, therefore, be profitably employed to elucidate the state of chemical equilibrium in the solution. For this purpose the determination of C_β by the equation

$$C_\beta = \frac{e^{\frac{Q}{R} \left(\frac{1}{T_0} - \frac{1}{T} \right)}}{(\nu-1)(1-x)} - \frac{1}{\nu-1} \dots \dots \dots (53)$$

seems to be the most convenient. That ν must be found by trial is the weak point in this method. But when its value is once determined, C_α and \mathfrak{K} can readily be found. For the determination of the characteristic quantities ν , \mathfrak{D} , and \mathfrak{T} three fusion points are necessary.

(2) *The Solid is the Associated Component.*

Of which chemical species the solid phase of the associated substance consists is a matter of indifference, because the heat of dissociation or association will be included in the heat of fusion as it is observed or calculated. But it is otherwise when the solid phase consists of the mixture of the two chemical species \mathfrak{S}_α and \mathfrak{S}_β . In this case the heat of fusion must vary with the temperature on account of the variation of the degree of association in the solid phase. As this consideration leads to a tolerably complicated result, we shall not discuss it in this place.

In the following we shall consider the solid phase to be in immediate relation to the chemical species \mathfrak{S}_β in the solution. Then we have by equation (17)

$$C_\beta = e^{\frac{Q'}{R} \left(\frac{1}{T_0} - \frac{1}{T} \right)} \dots \dots \dots (54)$$

where Q' is the molecular heat of fusion of the solid to a liquid consisting of pure \mathfrak{S}_β , and T'_0 is the hypothetical fusion point. From equations (32), and (54) we get

$$C_\alpha = e^{\frac{\mathfrak{D}}{\nu R} \left(\frac{1}{\mathfrak{T}} - \frac{1}{T} \right) + \frac{Q'}{\nu R} \left(\frac{1}{T'_0} - \frac{1}{T} \right)}$$

But as

$$x = \frac{1 - C_\alpha - C_\beta}{1 + (\nu - 1) C_\beta}$$

we have

$$x = \frac{1 - e^{\frac{\mathfrak{D}}{\nu R} \left(\frac{1}{\mathfrak{T}} - \frac{1}{T} \right) + \frac{Q'}{\nu R} \left(\frac{1}{T'_0} - \frac{1}{T} \right)} - e^{\frac{Q'}{R} \left(\frac{1}{T'_0} - \frac{1}{T} \right)}}{1 + (\nu - 1) e^{\frac{Q'}{R} \left(\frac{1}{T'_0} - \frac{1}{T} \right)}} \dots\dots(55)$$

This is the equation of the fusion curve of the associated component under the supposition made. This equation has also been tested by YAMAMOTO for the fusion curve of phenol in the above mentioned system, but it has not been found in satisfactory agreement with observations. Whether solid phenol is a mixture of two or more chemical species, or whether the data employed in the calculation are at fault can not be determined. The subject evidently requires more thorough study.

§ 3. Systems with one Associated and two Normal Components.

(a) *Homogeneous Equilibrium.*

In the present case we have four chemical species \mathfrak{S}_α , \mathfrak{S}_β , \mathfrak{S}_1 , and \mathfrak{S}_2 , the last two of which are normal substances. Their molar fractions must satisfy the following equation :

$$C_\alpha + C_\beta + C_1 + C_2 = 1 \dots\dots\dots(56)$$

It is quite clear that the chemical species \mathfrak{S}_1 and \mathfrak{S}_2 are symmetrically related to the other chemical species. If we put

$$C_1 + C_2 = C,$$

we get quite the same equations as in the foregoing section, and the relations found there must apply to the present case without any alterations.

Now let the empirical molar fraction of the associated component be x , and those of the normal components, y and z ; then we have

$$x = \frac{C_\alpha + \nu C_\beta}{C_\alpha + \nu C_\beta + C_1 + C_2} = \frac{C_\alpha + \nu C_\beta}{1 + (\nu - 1) C_\beta} \dots\dots\dots(57)$$

$$y = \frac{C_1}{1 + (\nu - 1) C_\beta} \dots\dots\dots(58)$$

$$z = \frac{C_2}{1 + (\nu - 1) C_\beta} \dots\dots\dots(59)$$

and $x + y + z = 1$.

These equations together with (30) enable us to determine C_α , C_β , C_1 , and C_2 as functions of the empirical molar fractions. As C_β must have a constant value for $C_1 + C_2 = C = \text{constant}$, it follows from (58) and (59) that $y + z = \text{constant}$. But this is equivalent to $x = \text{constant}$. The surfaces of C_α and C_β must therefore have the forms represented in Figs. 15 and 16. The loci of the points

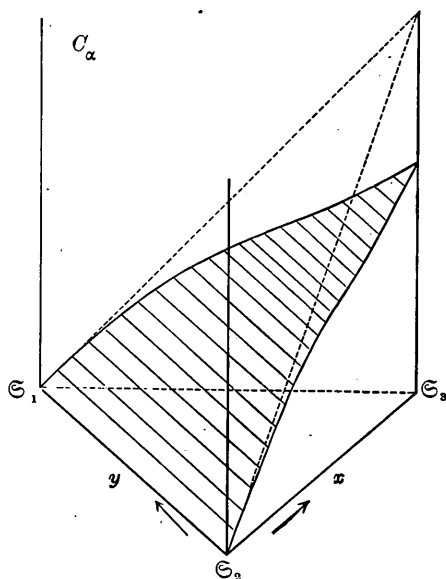


Fig. 15.

on the surfaces having equal values must be straight lines parallel to the axis of y . The projections of these loci upon the plane of composition may be called equifractional curves. In the present case they may also be called equipotential curves, because they are the loci of points at which the chemical potential has equal values. These are of course straight lines parallel to the axis of y .

The surfaces of C_1 and C_2 are perfectly similar, hence we need consider but one of them. The surface is bounded on one side by the binary curve Fig. 12 γ , and on the other by a straight line as shown in the annexed diagram. On solving equation (57) C_β can be obtained as an explicit function of \mathfrak{D} , \mathfrak{T} , T , and x ; and the equation for the surface of C_1 has the following form

$$C_1 = y\{1 + (\nu - 1)\varphi(\mathfrak{D}, \mathfrak{T}, T, x)\} \dots (60)$$

As C_β is independent of y we have for constant C_1

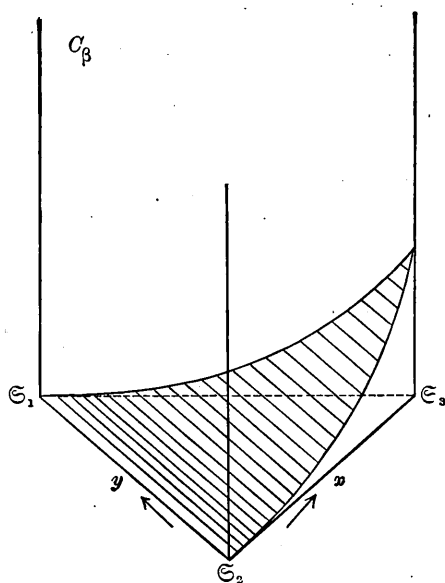


Fig. 16.

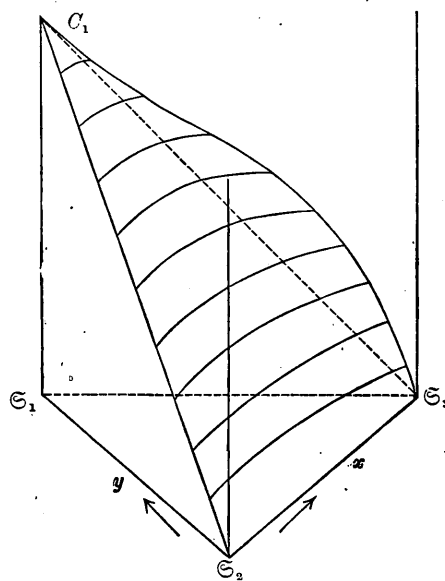


Fig. 17.

$$\frac{dy}{dx} = -\frac{(\nu-1) C_1 \frac{\partial C_\beta}{\partial x}}{\{1 + (\nu-1) C_\beta\}^2} \dots\dots\dots(61)$$

We have seen by equation (39) that $\frac{\partial C_\beta}{\partial x}$ is always positive, hence

$$\frac{dy}{dx} < 0.$$

Only at $x = 0$, $\frac{\partial C_\beta}{\partial x} = 0$, hence

$$\left(\frac{dy}{dx}\right)_0 = 0,$$

while at the other end where $z = 0$,

$$\frac{dy}{dx} = -\frac{(\nu-1) C_1}{\nu + \frac{C_\alpha}{\nu C_\beta} - \frac{(\nu-1)^2}{\nu} C_\alpha} < 0.$$

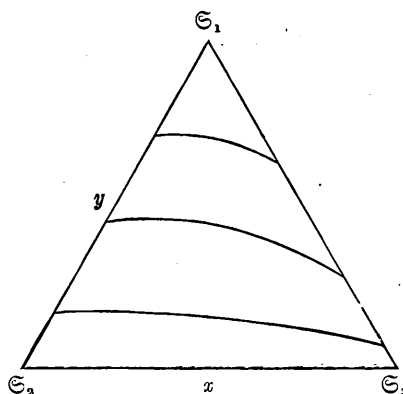


Fig. 18.

The equifractional curve for C_1 must, therefore, have a form shown in Fig. 18, being concave to the axis of x at least for the smaller values of x .

(b) *The Equilibrium between Gaseous and Liquid Phases.*

As the form of the surfaces of the partial vapour pressures at a constant temperature can be readily deduced from the surfaces of the molar fractions we need not describe them in this place. As to the surface of the total pressure it is represented by the equation

$$P = \pi_\alpha C_\alpha + \pi_\beta C_\beta + \pi_1 C_1 + \pi_2 C_2,$$

which may be written

$$P = \pi_{\alpha} C_{\alpha} + \pi_{\beta} C_{\beta} + \{1 + (\nu - 1) C_{\beta}\} \{\pi_1 y + \pi_2 (1 - x - y)\}$$

$$\text{or } P = \pi_{\alpha} C_{\alpha} + \pi_{\beta} C_{\beta} + \{1 + (\nu - 1) C_{\beta}\} (1 - x) \pi_2 + \{1 + (\nu - 1) C_{\beta}\} (\pi_1 - \pi_2) y.$$

As C_{α} and C_{β} are independent of y , only the last term is variable in the right side of this equation, when x is made constant. Hence planes erected perpendicular to the plane of composition and parallel to the axis of y must cut the surface of the total pressure in straight lines. This surface is therefore

a ruled surface as shown in

Fig. 19. As $\frac{\partial C_{\beta}}{\partial x}$ is positive

the inclination of the straight lines must increase with increasing x . The system ethyl

alcohol—benzene—carbon tetrachloride studied by SCHREINEMAKERS (Zeit. physik. Chem.,

47, 445; 1904) appears to be in qualitative agreement with the foregoing result. Yet the

mutual relation between the alcohol and the normal com-

ponents seems to be more complicated, the decrease of the chemical potential on mixing being less than might be expected, were the conditions of the quasi-ideal solutions fulfilled.

The relation between the boiling point and the composition will not be discussed in this place, because it is rather complicated and there seems at present to be but scanty field for application of the results to be obtained.

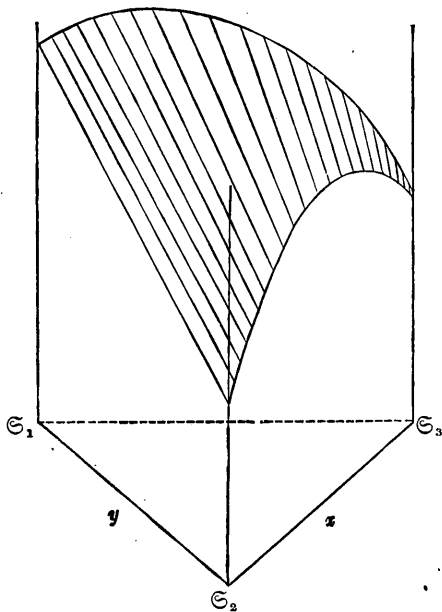


Fig. 19.

(c) *The Equilibrium between Liquid and Solid Phases.*

(1) *Solubility Curves.*

Let us first take the case in which the solid phase is a normal component; and as the two normal components must show quite similar relations it is enough to consider only one of them. According to equation (17) the molar fraction of \mathfrak{S}_1 in a solution, which is in equilibrium with the solid \mathfrak{S}_1 , must be constant at a constant temperature. The solubility curves of \mathfrak{S}_1 must therefore have the same form as the equifractional curve shown in Fig. 18. This has been verified by H. HIROBE¹⁾ in the solubility curves of naphthalene in the system phenol-naphthalene-chlorobenzene. Equation (61) has been found to represent the solubility curves with tolerable approximation, the deviation in the value of x not exceeding 0.015.

When the solid phase is the associated component the solubility curves must be straight lines parallel to the axis of y , as the equifractional curves of C_β as well as those of C_α are such. HIROBE has found that the solubility curves of phenol in the system at various temperatures almost exactly fulfill this requirement.

We have seen in § 3 (a) of the preceding chapter that the solubility curves of a component in an ideal solution are straight lines parallel to one of the axes. But we are not justified in concluding from such a course of a solubility curve that the solution is an ideal one, because this is but a consequence of a symmetrical relation between the components. When two components are symmetrically related to a third the solubility curve of the latter must necessarily be such a straight line.

1) See Art. 12 of this Volume.

(2) *Fusion Surfaces.*

The equation for the fusion surface of a normal component can be obtained by expressing C_1 in equation (60) as a function of temperature. Hence from (17) we have

$$y \{1 + (\nu - 1) \varphi(\mathfrak{D}, \mathfrak{T}, T, x)\} = e^{\frac{Q}{R} \left(\frac{1}{T_1} - \frac{1}{T} \right)}.$$

This equation has been found by HIROBE¹⁾ to represent the fusion surface of naphthalene with tolerable approximation, the temperature of fusion calculated differing by not more than 1° from the observed values.

The fusion surface of the associated component will be represented by equation (55), because the fusion point is quite independent of y . In the system studied by HIROBE the fusion surface of phenol is nearly a plane, which deviates considerably from the calculated surface.

1) Loc. cit.

