CHAPTER 4

MIXTURES

§4.01 *Introduction*

In this chapter we shall discuss homogeneous mixtures of two or more substances which do not react chemically. Consideration of chemical reactions is postponed to chapter 6. The mixtures may be gaseous, liquid, or solid. So far as possible each of the several component substances of a mixture will be treated on the same basis. The opposite point of view is taken in chapter 5 where one substance is regarded as the solvent and the remaining substances as solutes.

As soon as we turn from single substances to mixtures we introduce the possibility of new degrees of freedom associated with differences of composition. For example we can have two or more liquid phases of different composition in mutual equilibrium.

There are no differences of principle between the treatments of systems of two components on the one hand and of systems of more than two components on the other. Many of the formulae for the former are however more compact than the corresponding formulae for the latter. For this reason we shall in some sections confine ourselves mainly if not entirely, to systems of two substances, i.e. *binary* systems.

§4.02 *Composition of mixture*

The most convenient quantities specifying the relative composition of a mixture are the mole fractions of the several components. These were defined in §1.29. We recall that in a mixture of c components only c−1 of the mole fractions are independent owing to the identity

$$x_1+x_2+\ldots+x_c=1. \qquad 4.02.1$$

When we require independent variables it is convenient to use $x_2, x_3, \ldots x_c$ and regard x_1 as a dependent variable defined by

$$x_1=1-x_2-x_3-\ldots-x_c. \qquad 4.02.2$$

In the simple case of a binary mixture the subscripts may be dropped so that we write x instead of x_2 and $1-x$ instead of x_1.

§4.03 *Partial and proper quantities*

We recall the definitions in §1.26 of partial quantities X_i and proper quantities X_m in terms of an extensive property X, namely

$$X_i = (\partial X/\partial n_i)_{T,P,n_j} \qquad (j \neq i) \qquad 4.03.1$$

$$X_m = X/\sum_i n_i. \qquad 4.03.2$$

We also recall formula (1.26.3)

$$X = \sum_i n_i X_i. \qquad 4.03.3$$

If we differentiate this we obtain

$$\mathrm{d}X = \sum_i X_i \mathrm{d}n_i + \sum_i n_i \mathrm{d}X_i \qquad 4.03.4$$

while (1) may be rewritten as

$$\mathrm{d}X = \sum_i X_i \mathrm{d}n_i \qquad (\text{const. } T, P). \qquad 4.03.5$$

Subtracting (5) from (4) we obtain

$$\sum_i n_i \mathrm{d}X_i = 0 \qquad (\text{const. } T, P) \qquad 4.03.6$$

or dividing by $\Sigma_i n_i$

$$\sum_i x_i \mathrm{d}X_i = 0 \qquad (\text{const. } T, P). \qquad 4.03.7$$

In particular for a binary mixture

$$(1-x)(\partial X_1/\partial x) + x(\partial X_2/\partial x) = 0 \qquad (\text{const. } T, P). \qquad 4.03.8$$

In the case of a binary mixture we can express X_1 and X_2 in terms of X_m and x. Formula (5) reduces to

$$\mathrm{d}X = X_1 \mathrm{d}n_1 + X_2 \mathrm{d}n_2. \qquad 4.03.9$$

If we apply (9) to unit amount of varying composition, it becomes

$$\mathrm{d}X_m = (X_2 - X_1)\mathrm{d}x \qquad 4.03.10$$

or

$$(\partial X_m/\partial x)_{T,P} = X_2 - X_1. \qquad 4.03.11$$

If we apply (3) to unit amount it becomes

$$X_m = (1-x)X_1 + xX_2. \tag{4.03.12}$$

Solving (11) and (12) for X_1 and X_2 we obtain

$$X_1 = X_m - x(\partial X_m/\partial x)_{T,P} \tag{4.03.13}$$

$$X_2 = X_m + (1-x)(\partial X_m/\partial x)_{T,P}. \tag{4.03.14}$$

Formulae (13) and (14) have a simple geometrical interpretation shown in figure 4.1. The abscissa is x, increasing from zero at O representing the pure component 1 to unity at O′ representing the pure component 2. Suppose the curve APB to be a plot of the proper quantity X_m as ordinate and P to be any point on it. Let the tangent QPR to this curve at P cut the O and O′ ordinates at Q and R respectively. Then from (13) and (14) we see that the partial quantities X_1 and X_2 for the composition at P are represented by OQ and O′R respectively. It is clear from this construction or otherwise that for either pure component the partial quantity is equal to the proper quantity.

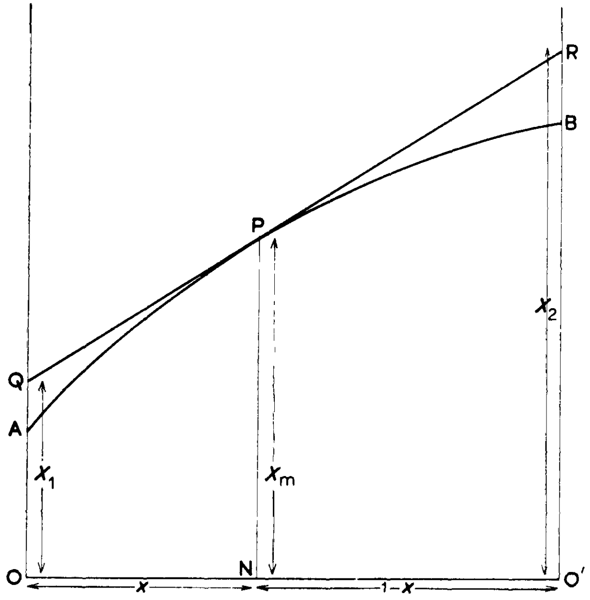

Fig. 4.1. Relation between partial quantities and proper quantity

An especially important example of the pair of formulae (13) and (14) is obtained by setting $X = G$. Taking account of (1.28.11) we obtain

$$\mu_1 = G_1 = G_\mathrm{m} - x(\partial G_\mathrm{m}/\partial x)_{T,P} \qquad 4.03.15$$

$$\mu_2 = G_2 = G_\mathrm{m} + (1-x)(\partial G_\mathrm{m}/\partial x)_{T,P}. \qquad 4.03.16$$

§ 4.04 *Relations between partial quantities*

As already mentioned in § 1.26 from every homogeneous relation between extensive properties we obtain by differentiation with respect to n_i a corresponding relation between the partial quantities at a given composition. We now give important examples of such relations taking into account (1.28.11) that

$$\mu_i = G_i. \qquad 4.04.1$$

We have with T, P as independent variables

$$H_i = U_i + PV_i \qquad 4.04.2$$

$$\mu_i = G_i = U_i - TS_i + PV_i \qquad 4.04.3$$

$$S_i = -\partial G_i/\partial T = -\partial \mu_i/\partial T \qquad 4.04.4$$

$$H_i = G_i - T\partial G_i/\partial T = \mu_i - T\partial \mu_i/\partial T \qquad 4.04.5$$

$$V_i = \partial G_i/\partial P = \partial \mu_i/\partial P \qquad 4.04.6$$

$$C_i = T\partial S_i/\partial T = \partial H_i/\partial T. \qquad 4.04.7$$

Relations of precisely the same form hold between proper quantities.

From (5) and (3.15.2) we deduce

$$\partial \ln \lambda_i/\partial T = -H_i/RT^2. \qquad 4.04.8$$

§ 4.05 *Partial quantities at high dilution*

By rewriting (4.03.8) in the form

$$(\partial X_1/\partial x)/(\partial X_2/\partial x) = -x/(1-x) \qquad 4.05.1$$

we make the interesting observation that as $x \to 0$ either $(\partial X_1/\partial x) \to 0$ or $(\partial X_2/\partial x) \to \infty$. Both alternatives occur. We shall find that as $x \to 0$, the quantities $(\partial U_1/\partial x)$, $(\partial H_1/\partial x)$, $(\partial V_1/\partial x)$, $(\partial C_1/\partial x)$ all tend towards zero, while $(\partial S_2/\partial x)$ and $(\partial G_2/\partial x) = (\partial \mu_2/\partial x)$ tend to infinity.

In the limit $x \to 1$ we of course meet the converse behaviour.

§ 4.06 *Perfect gaseous mixture*

In discussing gaseous mixtures, or in discussing single gases, it is expedient to begin by taking T, V as independent variables and later to transform to T, P as independent variables.

We begin by rewriting some of the most important formulae for an amount n of a single perfect gas occupying a volume V at a temperature T. The Helmholtz function is

$$ᶏ = n\{\mu^{\ominus} - RT + RT \ln(nRT/P^{\ominus}V)\} \qquad 4.06.1$$

where $\mu^{\ominus}$ depends on T and on the standard pressure $P^{\ominus}$ but not on n or V. From (1) we derive by differentiation

$$S = -n\{\mathrm{d}\mu^{\ominus}/\mathrm{d}T + R \ln(nRT/P^{\ominus}V)\} \qquad 4.06.2$$

$$U = n\{\mu^{\ominus} - T\,\mathrm{d}\mu^{\ominus}/\mathrm{d}T - RT\} \qquad 4.06.3$$

$$P = nRT/V \qquad 4.06.4$$

$$H = n\{\mu^{\ominus} - T\,\mathrm{d}\mu^{\ominus}/\mathrm{d}T\} \qquad 4.06.5$$

$$G = n\{\mu^{\ominus} + RT \ln(nRT/P^{\ominus}V)\} = n\{\mu^{\ominus} + RT \ln(P/P^{\ominus})\}. \qquad 4.06.6$$

Formula (6) may be regarded as defining $\mu^{\ominus}$.

We now define a perfect gaseous mixture by the property that at given T, V the Helmholtz function ᶏ of the mixture is equal to the sum of the Helmholtz functions of the unmixed gases each at the given T, V. We accordingly have for a perfect gaseous mixture

$$ᶏ = \sum_i n_i\{\mu_i^{\ominus} - RT + RT \ln(n_i RT/P^{\ominus}V)\}. \qquad 4.06.7$$

The molecular interpretation of formula (7) is that for a mixture of perfect gases in a container at given temperature and volume the molecules of each gaseous species behave as if the other species were absent. From the additivity of the Helmoltz function we deduce by differentiation the additivity of other functions. In particular we have

$$S = -\sum_i n_i\{\mathrm{d}\mu_i^{\ominus}/\mathrm{d}T + R \ln(n_i RT/P^{\ominus}V)\} \qquad 4.06.8$$

$$U = \sum_i n_i\{\mu_i^{\ominus} - T\,\mathrm{d}\mu_i^{\ominus}/\mathrm{d}T - RT\} \qquad 4.06.9$$

$$P = \sum_i n_i RT/V \qquad 4.06.10$$

$$H = \sum_i n_i\{\mu_i^{\ominus} - T\,\mathrm{d}\mu_i^{\ominus}/\mathrm{d}T\} \qquad 4.06.11$$

$$G = \sum_i n_i\{\mu_i^{\ominus} + RT \ln(n_i RT/P^{\ominus}V)\}$$

$$= \sum_i n_i\{\mu_i^{\ominus} + RT \ln(x_i P/P^{\ominus})\}. \qquad 4.06.12$$

We repeat that $\mu_i^\ominus$ is a function of T and $P^\ominus$ independent of V and the n_i's.

Formula (10) is called *Dalton's law of partial pressures*; a better name would be the *law of additivity of pressures.*

§ 4.07 *Slightly imperfect gaseous mixture*

A single gas or a gaseous mixture may be regarded as perfect if the interactions between molecules may be neglected. When these interactions between molecules are not negligible we use a *virial expansion* in powers of n/V. We recall the formulae for a single gas

$$\begin{aligned}\mathcal{F} = n\{\mu^\ominus - RT + RT\ln(nRT/P^\ominus V)\}\\ + nRT\{nB_2/V + \tfrac{1}{2}n^2B_3/V^2 + \tfrac{1}{3}n^3B_4/V^3\}\end{aligned} \qquad 4.07.1$$

where B_2, B_3, and B_4 are the second, third, and fourth virial coefficients respectively. Higher terms may be added, but when three virial coefficients are insufficient the virial expansion ceases to be useful.

From (1) we obtain by differentiation with respect to V

$$P = (nRT/V)\{1 + nB_2/V + n^2B_3/V^2 + n^3B_4/V^3\}. \qquad 4.07.2$$

Either formula (1) or formula (2) defines the virial coefficients B_2, B_3, B_4. For the sake of brevity and simplicity we shall omit the terms in B_3, B_4. There is in principle no difficulty in including them if required. We accordingly abbreviate (1) to

$$\mathcal{F} = n\{\mu^\ominus - RT + RT\ln(nRT/P^\ominus V)\} + n^2B/V \qquad 4.07.3$$

where we have dropped the subscript 2 from B_2.

It is known from statistical mechanics that B_2 takes account of interactions between pairs of molecules, B_3 between triplets, B_4 between quadruplets. This tells us how to generalize formula (1) to mixtures. In particular for a binary mixture

$$\begin{aligned}\mathcal{F} = n_1\{\mu_1^\ominus - RT + RT\ln(n_1RT/P^\ominus V)\}\\ + n_2\{\mu_2^\ominus - RT + RT\ln(n_2RT/P^\ominus V)\}\\ + \{n_1^2B_{(11)} + 2n_1n_2B_{(12)} + n_2^2B_{(22)}\}RT/V.\end{aligned} \qquad 4.07.4$$

Differentiating (4) with respect to V we obtain

$$PV = (n_1+n_2)RT + \{n_1^2B_{(11)} + 2n_1n_2B_{(12)} + n_2^2B_{(22)}\}RT/V. \qquad 4.07.5$$

From (4) and (5) we obtain by addition for the Gibbs function

$$\begin{aligned}G = n_1\{\mu_1^\ominus + RT\ln(n_1RT/P^\ominus V)\}\\ + n_2\{\mu_2^\ominus + RT\ln(n_2RT/P^\ominus V)\}\\ + 2\{n_1^2B_{(11)} + 2n_1n_2B_{(12)} + n_2^2B_{(22)}\}RT/V.\end{aligned} \qquad 4.07.6$$

If we may neglect terms in the squares of $B_{(11)}$, $B_{(12)}$, $B_{(22)}$ as well as terms in the third and higher virial coefficients, we call the mixture *slightly* imperfect. From (5) we have to this approximation

$$\ln(PV/RT)=\ln(n_1+n_2)+\{n_1^2B_{(11)}+2n_1n_2B_{(12)}+n_2^2B_{(22)}\}/(n_1+n_2)V. \qquad 4.07.7$$

Substituting from (7) into (6) we obtain

$$\begin{aligned}G=\,&n_1\{\mu_1^\ominus+RT\ln(P/P^\ominus)+RT\ln[n_1/(n_1+n_2)]\}\\&+n_2\{\mu_2^\ominus+RT\ln(P/P^\ominus)+RT\ln[n_2/(n_1+n_2)]\}\\&+\{n_1^2B_{(11)}+2n_1n_2B_{(12)}+n_2^2B_{(22)}\}P/(n_1+n_2)\end{aligned} \qquad 4.07.8$$

and consequently for the proper Gibbs function

$$\begin{aligned}G_\mathrm{m}=\,&x_1\{\mu_1^\ominus+RT\ln(P/P^\ominus)+RT\ln x_1\}\\&+x_2\{\mu_2^\ominus+RT\ln(P/P^\ominus)+RT\ln x_2\}\\&+\{x_1^2B_{(11)}+2x_1x_2B_{(12)}+x_2^2B_{(22)}\}P.\end{aligned} \qquad 4.07.9$$

It is convenient to define a quantity $\delta_{(12)}$ by

$$B_{12}=\tfrac{1}{2}(B_{(11)}+B_{(22)})+\delta_{(12)}. \qquad 4.07.10$$

We can now rewrite (9) as

$$\begin{aligned}G_\mathrm{m}=\,&x_1\{\mu_1^\ominus+RT\ln(P/P^\ominus)+RT\ln x_1+B_{(11)}P\}\\&+x_2\{\mu_2^\ominus+RT\ln(P/P^\ominus)+RT\ln x_2+B_{(22)}P\}\\&+2x_1x_2\delta_{(12)}P.\end{aligned} \qquad 4.07.11$$

Experimental data on $B_{(12)}$ or $\delta_{(12)}$ are much scantier than data on $B_{(11)}$ and $B_{(22)}$. When the species 1 and 2 conform to the principle of corresponding states it is possible to estimate $B_{(12)}$ from $B_{(11)}$ and $B_{(22)}$ with useful accuracy*. When this is not the case it is usual to neglect $\delta_{(12)}$. This procedure is due to Lewis and Randall†.

From (11) by use of (4.03.13) and (4.03.14) we deduce

$$RT\ln\lambda_1=\mu_1=G_1=\mu_1^\ominus+RT\ln(P/P^\ominus)+RT\ln x_1+(B_{11}+2x_2^2\delta_{(12)})P \qquad 4.07.12$$

$$RT\ln\lambda_2=\mu_2=G_2=\mu_2^\ominus+RT\ln(P/P^\ominus)+RT\ln x_2+(B_{22}+2x_1^2\delta_{(12)})P. \qquad 4.07.13$$

By further differentiations we obtain

$$-S_1=\mathrm{d}\mu_1^\ominus/\mathrm{d}T+R\ln(P/P^\ominus)+R\ln x_1+(\mathrm{d}/\mathrm{d}T)(B_{11}+2x_2^2\delta_{(12)})P \qquad 4.07.14$$

* Guggenheim and McGlashan, Proc. Roy. Soc. A 1951 **206** 448.

† Lewis and Randall, Thermodynamics and the Free Energy of Chemical Substances, McGraw-Hill 1923 p. 226.

$$H_1=\mu_1^{\ominus}-T\mathrm{d}\mu_1/\mathrm{d}T+(1-T\mathrm{d}/\mathrm{d}T)(B_{11}+2x_2^2\delta_{(12)})P \qquad 4.07.15$$

$$V_1=RT/P+B_{11}+2x_2^2\delta_{(12)}. \qquad 4.07.16$$

There are analogous formulae for S_2, H_2, and V_2.

§4.08 *Fugacities of gases*

The fugacity p_i of each species i in a gas is defined by

$$p_i/\lambda_i=\text{const.} \qquad (T\text{ const.}) \qquad 4.08.1$$

$$p_i/x_iP\rightarrow 1 \quad \text{as} \quad P\rightarrow 0 \qquad (T\text{ const.}). \qquad 4.08.2$$

Using these definitions we obtain for a binary mixture from (4.07.12) and (4.07.13)

$$p_1=x_1P\exp\{(B_{11}+2x_2^2\delta_{(12)})P/RT\} \qquad 4.08.3$$

$$p_2=x_2P\exp\{(B_{22}+2x_1^2\delta_{(12)})P/RT\}. \qquad 4.08.4$$

The quantity x_iP is called the *partial pressure* of i.

In a perfect gas these simplify to

$$p_1=x_1P \qquad 4.08.5$$

$$p_2=x_2P \qquad 4.08.6$$

so that the fugacity of each species is equal to its partial pressure.

§4.09 *Liquid mixtures*

We now turn to liquid mixtures and the equilibrium between such phases and other phases, especially a gas phase. We begin by certain general considerations applying to all such liquid mixtures. We shall next consider a special class of such mixtures, called *ideal*, which exhibit an especially simple behaviour. We shall then show how the behaviour of non-ideal mixtures can conveniently be compared and correlated with that of ideal mixtures. The procedure will be illustrated in greater detail for a class of mixtures called *simple*.

§4.10 *Liquid–vapour equilibrium*

Let us now consider from a general point of view the equilibrium conditions between a liquid mixture of c independent species or components and a vapour phase. Each phase by itself has evidently c+1 degrees of freedom, which we can take as given by the c+1 independent variables T, P, x_2, x_3, ... x_c. Alternatively if we use the c+2 variables T, P, μ_1, μ_2, ... μ_c these are not independent, being connected by the Gibbs–Duhem relation

$$S_m dT - V_m dP + x_1 d\mu_1 + x_2 d\mu_2 + \ldots + x_c d\mu_c = 0. \qquad 4.10.1$$

We now consider two phases, one liquid and the other vapour, in mutual equilibrium. We shall continue to use x_i to denote a mole fraction in the liquid phase but shall henceforth denote a mole fraction in the vapour phase by y_i. The variables T, P, μ_1, μ_2, ... μ_c are connected by two Gibbs–Duhem relations, one for each phase. Thus, using the superscripts ^{L} to denote liquid and ^{G} to denote gas, we have

$$S_m^L dT - V_m^L dP + x_1 d\mu_1 + x_2 d\mu_2 + \ldots + x_c d\mu_c = 0 \qquad 4.10.2$$

$$S_m^G dT - V_m^G dP + y_1 d\mu_1 + y_2 d\mu_2 + \ldots + y_c d\mu_c = 0. \qquad 4.10.3$$

It is hardly necessary to point out that we need not attach superscripts to the variables T, P, μ_1, μ_2, ... μ_c since at equilibrium each of these has the same value in both phases.

From (2) and (3) we could, if we wished, eliminate any one of the quantities dT, dP, $d\mu_1$, $d\mu_2$, ... $d\mu_c$ thus obtaining a single relation between the remaining c+1 quantities. Whether we do this or not, it is clear that only c of these quantities are independent. We conclude that a system of two phases and c component species in equilibrium has c degrees of freedom in agreement with Gibbs' phase rule.

§ 4.11 *Azeotropy*

For a binary liquid–vapour system the relations (4.10.2) and (4.10.3) reduce to

$$S_m^L dT - V_m^L dP + (1-x) d\mu_1 + x d\mu_2 = 0 \qquad 4.11.1$$

$$S_m^G dT - V_m^G dP + (1-y) d\mu_1 + y d\mu_2 = 0 \qquad 4.11.2$$

where as usual x, y denote mole fractions of the second species. If we subtract (1) from (2) we obtain

$$(S_m^G - S_m^L) dT - (V_m^G - V_m^L) dP + (x-y)(d\mu_1 - d\mu_2) = 0. \qquad 4.11.3$$

We shall show that this leads to particularly simple and interesting results when the compositions of the two phases are the same, that is to say when

$$x = y. \qquad 4.11.4$$

Such mixtures are called *azeotropic*, which means that their composition is not changed by boiling.

Let us first consider variations of pressure and composition at constant temperature. Then (3) becomes

$$(V_\mathrm{m}^\mathrm{G}-V_\mathrm{m}^\mathrm{L})\mathrm{d}P/\mathrm{d}x=(x-y)(\mathrm{d}\mu_1/\mathrm{d}x-\mathrm{d}\mu_2/\mathrm{d}x) \qquad (\text{const. } T). \qquad 4.11.5$$

Hence for an azeotropic mixture, according to (4)

$$(V_\mathrm{m}^\mathrm{G}-V_\mathrm{m}^\mathrm{L})\mathrm{d}P/\mathrm{d}x=0 \qquad (\text{const. } T). \qquad 4.11.6$$

and since $V_\mathrm{m}^\mathrm{G}\neq V_\mathrm{m}^\mathrm{L}$ it follows that

$$\mathrm{d}P/\mathrm{d}x=0 \qquad (\text{const. } T). \qquad 4.11.7$$

This tells us that at a given temperature the total vapour pressure of a binary liquid mixture is a maximum or a minimum at the composition of the azeotropic mixture.

Similarly if we consider variations of temperature and composition at constant pressure, then (3) becomes

$$-(S_\mathrm{m}^\mathrm{G}-S_\mathrm{m}^\mathrm{L})\mathrm{d}T/\mathrm{d}x=(x-y)(\mathrm{d}\mu_1/\mathrm{d}x-\mathrm{d}\mu_2/\mathrm{d}x) \qquad (\text{const. } P). \qquad 4.11.8$$

and consequently for an azeotropic mixture

$$(S_\mathrm{m}^\mathrm{G}-S_\mathrm{m}^\mathrm{L})\mathrm{d}T/\mathrm{d}x=0 \qquad (\text{const. } P). \qquad 4.11.9$$

Since $S_\mathrm{m}^\mathrm{G}\neq S_\mathrm{m}^\mathrm{L}$, it follows that

$$\mathrm{d}T/\mathrm{d}x=0 \qquad (\text{const. } P). \qquad 4.11.10$$

This tells us that at a given pressure the boiling temperature of a binary liquid mixture is a maximum or a minimum at the composition of the azeotropic mixture.

These conclusions are almost obvious when expressed by diagrams. For example figure 4.2 shows the boiling point T plotted against compositions of the two phases. For instance the points L and G represent the liquid and gas phases in equilibrium at one temperature; L′, G′ is another such pair and L″, G″ another. The point M represents liquid and gas of the same composition and in this example the equilibrium temperature or boiling point is a minimum.

Let us now consider simultaneous variation of temperature and pressure such that the mixture remains azeotropic. Returning to formula (3) and substituting the condition for azeotropy (4), we have

$$(S_\mathrm{m}^\mathrm{G}-S_\mathrm{m}^\mathrm{L})\mathrm{d}T-(V_\mathrm{m}^\mathrm{G}-V_\mathrm{m}^\mathrm{L})\mathrm{d}P=0 \qquad 4.11.11$$

which we can rewrite as

$$dP/dT = (S_m^G - S_m^L)/(V_m^G - V_m^L) = \Delta_e S/\Delta_e V \qquad 4.11.12$$

of the same form as Clapeyron's relation (3.37.3).

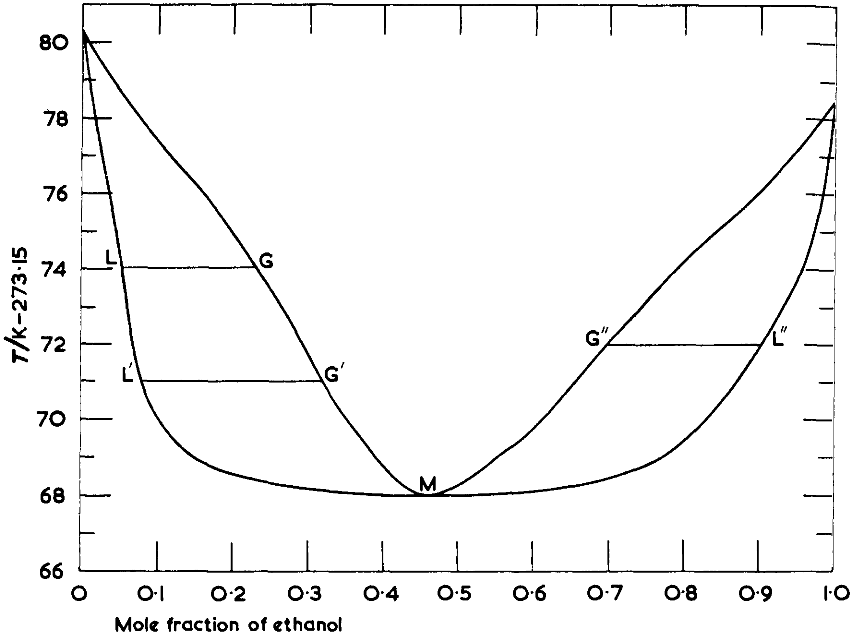

Fig. 4.2. Boiling point of mixtures of benzene and ethanol at one atmosphere

§4.12 *Relative activities and fugacities in liquids*

All the equilibrium properties of each species i are determined by its chemical potential μ_i or by its absolute activity λ_i related to μ_i by the definition

$$\mu_i = RT \ln \lambda_i. \qquad 4.12.1$$

Up to the present we have mentioned absolute activities from time to time and have given formulae for them with the object of familiarizing the reader with them. We have however hitherto made little use of absolute activities. Henceforth we shall make considerably increasing use of them, for in the treatment of mixtures they are often more convenient than chemical potentials.

In our consideration of liquid mixtures we shall be concerned particularly with a comparison of the equilibrium properties of the mixture with those of the pure components. Consequently we shall be concerned not so much with μ_i itself as with the difference $\mu_i - \mu_i^0$ where the superscript ^{0} denotes the value for the pure liquid at the same temperature and pressure. From (1) we have

$$\mu_i - \mu_i^0 = RT \ln(\lambda_i/\lambda_i^0) \qquad 4.12.2$$

where the superscript ^{0} is used again with the same meaning. We shall be particularly concerned with the ratios λ_i/λ_i^0. These ratios are called *relative activities* and will be denoted by a_i. This name and this symbol are due to G. N. Lewis*. We have then

$$a_i = \lambda_i/\lambda_i^0. \qquad 4.12.3$$

We must mention that quantities other than the relative activities defined here have sometimes also been called activities and denoted by the same symbol a_i. In order to avoid confusion we shall make no use or further mention of such other quantities.

For the equilibrium of the species i between any two phases α and β we have according to (3.15.6) the simple condition

$$\lambda_i^\alpha = \lambda_i^\beta \qquad 4.12.4$$

and in particular for the equilibrium between a liquid phase L and a gas phase G

$$\lambda_i^{\mathrm{L}} = \lambda_i^{\mathrm{G}}. \qquad 4.12.5$$

From (5) and (4.08.1) it follows that the ratio of the absolute activities of the species i in any two liquid phases α, β is equal to the ratio of the fugacities of the species in the gas phases in equilibrium with α, β respectively.

We now define the *fugacity* p_i of a species i in a liquid phase as follows. We begin by defining the fugacity p_i^0 of the pure liquid i at a given temperature as equal to the fugacity of its saturated vapour. We then define the fugacity of i in liquid mixtures at given temperatures but variable pressure and variable composition by

$$p_i/\lambda_i = \text{const.} \qquad (\text{const. } T). \qquad 4.12.6$$

An important application of (6) is to the comparison between the absolute activity λ_i of i in a liquid mixture and its absolute activity λ_i^0 in the pure liquid at the same temperature and pressure. We then have

$$a_i = \lambda_i/\lambda_i^0 = p_i/p_i^0. \qquad 4.12.7$$

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* Lewis, J. Amer. Chem. Soc. 1913 **35** 17.

§4.13 *Pressure dependence*

We must now describe how p_i is determined in a liquid mixture of given composition at a given temperature and at a given pressure. At the given temperature and composition we have to determine the total saturation vapour pressure P_{sat} and the composition of the vapour. If the vapour may be regarded as a perfect gas then the fugacity p_i is equal to the partial vapour pressure $y_i P_{\text{sat}}$. If the vapour is not a perfect gas we have to apply a correction for non-ideality by use of a formula such as (4.08.3). We then obtain the value of the fugacity at the given pressure P by means of

$$\partial \ln p_i/\partial P = \partial \ln \lambda_i/\partial P = V_i/RT \qquad 4.13.1$$

or in the integrated form

$$\ln p_i(P) - \ln p_i(P_{\text{sat}}) = (P - P_{\text{sat}})V_i/RT \qquad 4.13.2$$

where we have neglected compressibility.

Although at ordinary pressures the quantity on either side of (2) may be negligible, nevertheless formula (2) is in principle important as showing that $p_i(P)$ is precisely defined and precisely determinable for any chosen value of P, not merely for $P = P_{\text{sat}}$.

Formula (2) is also important in the discussion of osmotic equilibrium in the following section.

§4.14 *Osmotic equilibrium*

Suppose we have two liquid mixtures α and β separated by a membrane permeable to the species 1 but impermeable to all other species present in either mixture. In this connection we shall follow the customary practice of calling the permeant species 1 the *solvent* and the nonpermeant species *solutes*. We assume that the two phases are at the same temperature, but not necessarily at the same pressure. The condition that the two phases should be in equilibrium with respect to the solvent species 1 is

$$\lambda_1^{\alpha} = \lambda_1^{\beta} \qquad 4.14.1$$

or if we use (4.12.6)

$$p_1^{\alpha} = p_1^{\beta}. \qquad 4.14.2$$

For the relations to be satisfied it will generally be necessary for the two phases to be at different pressures. There is then equilibrium with respect to the solvent species 1, but not with respect to the solute species; nor is there hydrostatic equilibrium between the two phases, the difference of pressure being balanced by a force exerted by the membrane. A partial equilibrium of this kind is called *osmotic equilibrium* of the solvent species 1.

By using the relation (4.13.1)

$$\partial \ln p_1/\partial P = \partial \ln \lambda_1/\partial P = V_1/RT \qquad 4.14.3$$

we can determine the pressure $P^{\alpha} - P^{\beta}$ required to preserve osmotic equilibrium.

We shall use the notation $p_1(P, x)$ to denote the value of the fugacity of the solvent in a liquid phase of composition x at a pressure P. We do not refer to the temperature as this is assumed constant throughout. The condition (2) for osmotic equilibrium becomes in this notation

$$p_1(P^{\alpha}, x^{\alpha}) = p_1(P^{\beta}, x^{\beta}). \qquad 4.14.4$$

Dividing both sides of (4) by $p_1(P^{\beta}, x^{\alpha})$ and taking logarithms, we obtain

$$\ln\{p_1(P^{\alpha}, x^{\alpha})/p_1(P^{\beta}, x^{\alpha})\} = \ln\{p_1(P^{\beta}, x^{\beta})/p_1(P^{\beta}, x^{\alpha})\}. \qquad 4.14.5$$

If we integrate (3) from P^{β} to P^{α} and substitute the result on the left side of (5) we find

$$\frac{1}{RT}\int_{P^{\beta}}^{P^{\alpha}} V_1^{\alpha}\mathrm{d}P = \ln\{p_1(P^{\beta}, x^{\beta})/p_1(P^{\beta}, x^{\alpha})\}. \qquad 4.14.6$$

In order to evaluate the integral in (6) it is for most purposes sufficient to ignore compressibility and treat V_1 as independent of P. In case greater refinement should be desired, we can obtain all the accuracy that can ever be required by assuming that V_1 varies linearly with P. We then obtain

$$\langle V_1^{\alpha}\rangle(P^{\alpha} - P^{\beta})/RT = \ln\{p_1(P^{\beta}, x^{\beta})/p_1(P^{\beta}, x^{\alpha})\} \qquad 4.14.7$$

where the symbol $\langle V_1^{\alpha}\rangle$ denotes the value of V_1^{α} at a pressure equal to the mean of P^{α} and P^{β}.

Formula (7) is the general relation determining the pressure difference across the membrane at osmotic equilibrium. The case of greatest interest is when the phase β consists of the pure solvent. The pressure difference $P^{\alpha} - P^{\beta}$ is then called the *osmotic pressure* and is denoted by Π. We can in this case replace the superscript $^{\beta}$ by ^{0} and drop the superscript $^{\alpha}$. We thus have

$$\Pi\langle V_1\rangle/RT = \ln\{p_1^0(P)/p_1(P)\} \qquad 4.14.8$$

or if, as is often the case, we may ignore compressibility

$$\Pi V_1/RT = \ln\{p_1^0(P)/p_1(P)\}. \qquad 4.14.9$$

If moreover the pressure P on the pure solvent is roughly atmospheric, then regardlesss of how great Π may be we may regard p_1^0/p_1 as essentially independent of P. Formula (9) can then be simplified to

$$\Pi V_1/RT=\ln(p_1^0/p_1) \tag{4.14.10}$$

from which we see that, provided the pressure P on the pure solvent is low, the osmotic pressure Π does not depend significantly on P.

If instead of dividing both sides of (4) by $p_1(P^\beta, x^\alpha)$, we divide both sides by $p_1(P^\alpha, x^\beta)$ and otherwise proceed in the same way, we obtain instead of (7)

$$\langle V_1^\beta\rangle(P^\alpha-P^\beta)/RT=\ln\{p_1(P^\alpha, x^\beta)/p_1(P^\alpha, x^\alpha)\} \tag{4.14.11}$$

and instead of (8)

$$\Pi\langle V_1^0\rangle/RT=\ln\{p_1^0(P+\Pi)/p_1(P+\Pi)\}. \tag{4.14.12}$$

It can be shown that the alternative formulae (8) and (12) are equivalent. On the whole formula (8) is the more useful.

§4.15 *Pressure on semi-permeable membrane*

The osmotic pressure is by definition a pressure that must be applied to the solution to bring it into a certain equilibrium condition. It is not a pressure exerted by the solution or part of the solution at its normal low pressure. It is analogous to the freezing point of a solution, which has no relation to the actual temperature of the solution, but is the temperature to which it must be brought to reach a certain equilibrium state. The osmotic pressure is nevertheless sometimes defined as the pressure exerted on a membrane, permeable only to the solvent, separating the solution from pure solvent. This definition, unless carefully qualified, is incorrect. Another definition sometimes given is the pressure exerted by the solute molecules on a membrane permeable only to the solvent. This definition is still more incorrect than the last. The truth as regards the pressure on the membrane is as follows. When the solution is at the same pressure e.g. atmospheric, as the solvent, there will be a resultant flow of solvent through the membrane from the solvent to the solution, but the resultant pressure on the membrane itself is negligibly small, and may be in either direction. If, however, the solution is subjected to a certain high external pressure, the flow of solvent through the membrane is equal in either direction; there is then osmotic equilibrium and the excess pressure on the solution over the pressure of the solvent is by definition the osmotic pressure. Under conditions of osmotic equilibrium, but only under these conditions, is the external pressure difference required to prevent the membrane from moving equal to the osmotic pressure.

§4.16 *Duhem–Margules relation*

We recall the Gibbs–Duhem relation

$$\sum_i n_i \mathrm{d}\mu_i = 0 \qquad \text{(const. } T, P) \qquad 4.16.1$$

or

$$\sum_i n_i \mathrm{d} \ln \lambda_i = 0 \qquad \text{(const. } T, P). \qquad 4.16.2$$

From (4.12.6) and (2) we deduce

$$\sum_i n_i \mathrm{d} \ln p_i = 0 \qquad \text{(const. } T, P) \qquad 4.16.3$$

or dividing by $\Sigma_i n_i$

$$\sum_i x_i \mathrm{d} \ln p_i = 0 \qquad \text{(const. } T, P). \qquad 4.16.4$$

This important relation is known as the *Duhem–Margules relation**.

In the simple case of a binary mixture (4) reduces to

$$(1-x)\partial \ln p_1/\partial x + x\partial \ln p_2/\partial x = 0 \qquad \text{(const. } T, P) \qquad 4.16.5$$

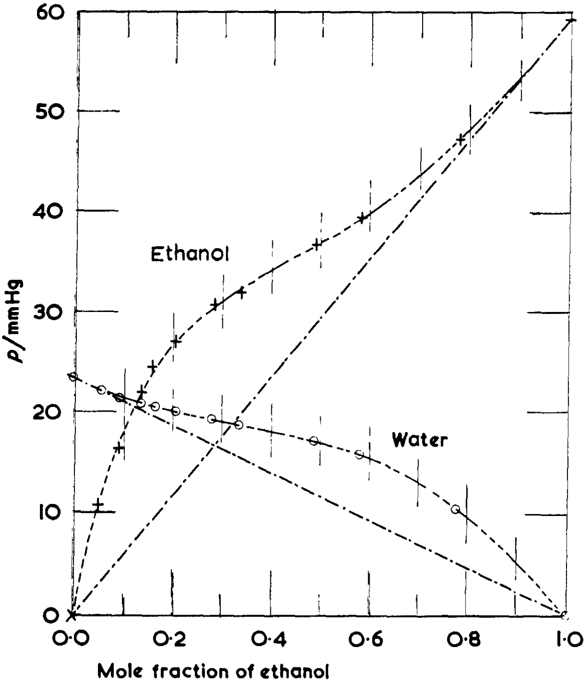

Fig. 4.3. Illustration of Duhem–Margules relation

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* Margules, Sitz. ber. Akad. Wiss. Wien 1895 **104** 1258–1260.

where as usual x denotes the mole fraction of species 2. It follows from this relation that if p_1 and p_2 are plotted against x, the shape of either curve completely determines the shape of the other. An example of this interrelation* between the pair of curves is shown in figure 4.3 and table 4.1, where the subscript $_1$ denotes water and $_2$ denotes ethanol. In this illustration no correction has been applied for gas imperfection. In other words p_1 has been taken as equal to $(1-y)P_{\text{sat}}$ and p_2 as equal to yP_{sat}.

TABLE 4.1

Verification of Duhem–Margules relation for mixtures of water and ethanol at 25 °C

x	$\dfrac{p_1 \approx (1-y)P_{\text{sat}}}{\text{mmHg}}$	$\dfrac{p_2 \approx y\,P_{\text{sat}}}{\text{mmHg}}$	$-(1-x)\,\partial \ln p_1/\partial x$ $=x\,\partial \ln p_2/\partial x$
0	23.75	0.0	1.00
0.1	21.7	17.8	0.76
0.2	20.4	26.8	0.41
0.3	19.4	31.2	0.37
0.4	18.35	34.2	0.355
0.5	17.3	36.9	0.41
0.6	15.8	40.1	0.53
0.7	13.3	43.9	0.655
0.8	10.0	48.3	0.77
0.9	5.5	53.3	0.915
1.0	0.0	59.0	1.00

§4.17 *Temperature coefficients*

Formula (4.04.5) is equivalent to

$$\partial(\mu_i/T)/\partial T = -H_i/T^2 \qquad 4.17.1$$

or

$$\partial \ln p_i/\partial T = -H_i/RT^2. \qquad 4.17.2$$

Consequently from (4.12.7)

$$\partial \ln a_i/\partial T = \partial \ln(p_i/p_i^0)/\partial T = -(H_i - H_i^0)/RT^2. \qquad 4.17.3$$

§4.18 *Ideal mixtures*

In order to obtain more detailed information concerning the equilibrium properties of liquid mixtures it is necessary to know or assume something

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* Adam and Guggenheim, Proc. Roy. Soc. A 1933 **139** 231.

about the dependence of the chemical potentials μ_i or the absolute activities λ_i on the composition of the mixture. Thermodynamic considerations alone cannot predict the form of this dependence, but only impose certain restrictions such as the Gibbs–Duhem relation.

We shall begin by considering liquid mixtures having the property that at constant temperature and pressure the dependence of the Gibbs function G, and consequently also of functions derived from G, on the composition is of the same form as for a perfect gaseous mixture. This means that the value of G in a mixture containing amount n_i of the species i exceeds the value of G for the unmixed species at the same temperature and pressure by the negative amount

$$\Delta G = RT \sum_i n_i \ln\{n_i/\sum_k n_k\}. \tag{4.18.1}$$

Such mixtures are called *ideal mixtures.* We shall devote considerable attention to such mixtures for several reasons.

In the first place the behaviour of ideal mixtures is the simplest conceivable either from a mathematical or from a physical aspect.

In the second place statistical theory predicts that mixtures of very similar species, in particular isotopes, will be ideal.

In the third place it is found experimentally that almost ideal mixtures exist, for example benzene + bromobenzene.

In the fourth place although real mixtures, other than isotopic mixtures, are not ideal, in many cases the resemblances between a real mixture and an ideal mixture are more striking than the differences.

§ 4.19 *Thermodynamic functions of ideal mixtures*

From formula (4.18.1) we can immediately derive formulae for all the thermodynamic functions of an ideal mixture. In particular we have, using the superscript ^{0} to refer to the pure liquids at the same pressure,

$$\mu_i = RT \ln \lambda_i = \partial G/\partial n_i = \mu_i^0 + RT \ln\{n_i/\sum_k n_k\} = \mu_i^0 + RT \ln x_i \tag{4.19.1}$$

$$a_i = \lambda_i/\lambda_i^0 = x_i \tag{4.19.2}$$

$$G_m = \sum_i x_i \mu_i = \sum_i x_i \mu_i^0 + RT \sum_i x_i \ln x_i \tag{4.19.3}$$

$$S_m = -\sum_i x_i \{\partial \mu_i^0/\partial T\} - R \sum_i x_i \ln x_i \tag{4.19.4}$$

$$H_m = \sum_i x_i \{\mu_i^0 - T(\partial \mu_i^0/\partial T)\} = \sum_i x_i H_i^0 \tag{4.19.5}$$

$$V_\mathrm{m}=\sum_i x_i\{\partial\mu_i^0/\partial P\}=\sum_i x_i V_i^0 \qquad 4.19.6$$

$$S_i=-\partial\mu_i^0/\partial T-R\ln x_i \qquad 4.19.7$$

$$H_i=\mu_i^0-T\{\partial\mu_i^0/\partial T\}=H_i^0 \qquad 4.19.8$$

$$V_i=\partial\mu_i^0/\partial P=V_i^0. \qquad 4.19.9$$

Furthermore if we use the symbol Δ_m to denote the increase in a function when unit amount of mixture is formed from the pure components at constant temperature and pressure we have

$$\Delta_\mathrm{m}G=RT\sum_i x_i\ln x_i \qquad 4.19.10$$

$$\Delta_\mathrm{m}S=-R\sum_i x_i\ln x_i \qquad 4.19.11$$

$$\Delta_\mathrm{m}H=0 \qquad 4.19.12$$

$$\Delta_\mathrm{m}V=0. \qquad 4.19.13$$

The relations (10), (11), (12), (13) have precisely the same form as for the formation of a perfect gaseous mixture from the pure component gases at constant temperature and pressure.

It must be emphasized that this similarity between ideal liquid mixtures and perfect gaseous mixtures as regards dependence of the thermodynamic properties on the composition holds only when the other independent variables are T and P. There are no correspondingly simple relations in terms of the variables T and V, which are moreover an inconvenient set of independent variables for any phase other than a gas.

There is, of course, no similarity between liquid and gaseous mixtures as regards dependence of properties on the pressure. For example, in a perfect gaseous mixture

$$\partial\mu_i/\partial P=V_i=RT/P \qquad 4.19.14$$

while in a liquid ideal mixture

$$\partial\mu_i/\partial P=\partial\mu_i^0/\partial P=V_i^0=V_i^{0\ominus}(1+\kappa P^\ominus-\kappa P) \qquad 4.19.15$$

where $V_i^{0\ominus}$ denotes the value of V_i^0 when $P=P^\ominus$ which varies only slightly with P.

§ 4.20 *Fugacities in ideal mixtures*

From formulae (4.08.1) and (4.19.2) we deduce immediately for each species in an ideal mixture

$$p_i = x_i p_i^0 \qquad \text{(const. } T;\ P\text{)}. \tag{4.20.1}$$

Since at ordinary pressures the equilibrium properties of a liquid are insensitive to the pressure, we may often with negligible error replace (1) by

$$p_i = x_i p_i^0 \qquad \text{(const. } T;\ P = P_{\text{sat}}\text{)} \tag{4.20.2}$$

where P_{sat} denotes the total pressure of the saturated vapour.

If moreover we may neglect deviations of the gas from ideality, we may replace each fugacity p_i by the partial pressure $y_i P$ so that (2) becomes

$$y_i P_{\text{sat}} = x_i P^0_{\text{sat},\,i} \qquad \text{(const. } T;\ P = P_{\text{sat}}\text{)} \tag{4.20.3}$$

where $P^0_{\text{sat},\,i}$ denotes the saturated vapour pressure of the pure liquid i. Formula (3) is called *Raoult's law.*

For a binary mixture (1) becomes

$$p_1 = (1-x)p_1^0 \qquad p_2 = x p_2^0 \qquad \text{(const. } T,\ P\text{)} \tag{4.20.4}$$

and formula (3) becomes

$$(1-y)P_{\text{sat}} = (1-x)P^0_{\text{sat},\,1} \qquad y P_{\text{sat}} = x P^0_{\text{sat},\,2} \qquad \text{(const. } T;\ P = P_{\text{sat}}\text{)}. \tag{4.20.5}$$

Thus if the fugacities, or less exactly the partial vapour pressures, of the two components of an ideal binary mixture are plotted against the mole fraction of one of them two straight lines are obtained. The experimental data* for the mixture ethylene bromide and propylene bromide at the temperature 85 °C are shown in figure 4.4 and we see that this mixture is

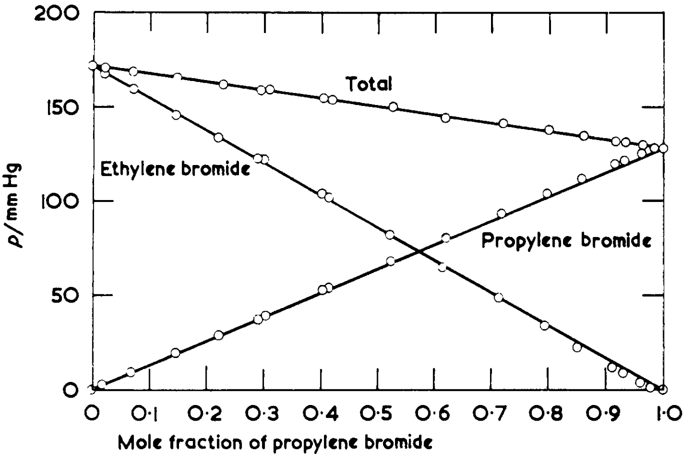

Fig. 4.4. Partial and total vapour pressures of mixtures of ethylene bromide and propylene bromide at 85 °C

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* Von Zawidzki, Z. Phys. Chem. 1900 **35** 129.

nearly ideal. In figure 4.5 we see a similar plot* for the mixture benzene and bromobenzene at 80 °C which is also nearly ideal in spite of the considerable difference between the vapour pressures of the two pure components.

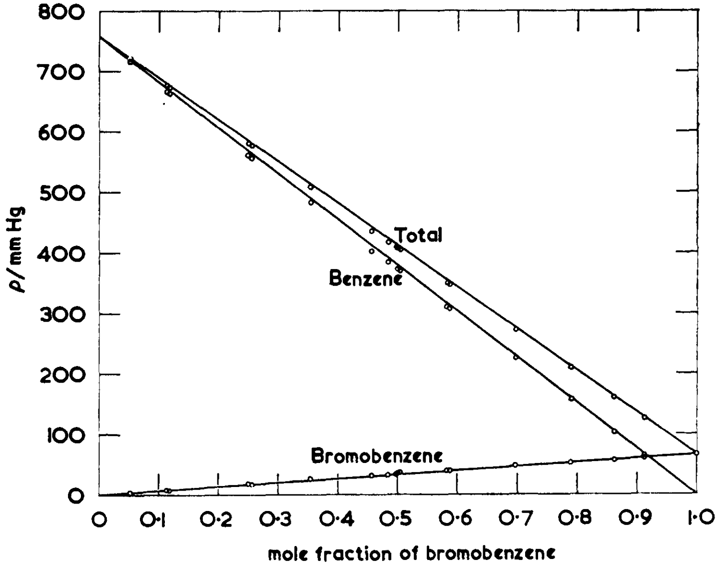

Fig. 4.5. Partial and total vapour pressures of mixtures of benzene and bromobenzene at 80 °C

§4.21 *Osmotic pressure of ideal solution*

To obtain the osmotic pressure of an ideal mixture or ideal solution, regarding the component 1 to which the membrane is permeable as solvent, we have merely to substitute (4.20.4) into (4.14.8). We thus obtain

$$\Pi\langle V_1\rangle/RT = -\ln x_1 \qquad 4.21.1$$

wherein we recall that $\langle V_1\rangle$ denotes the value of V_1 averaged between the pressures of the two phases in osmotic equilibrium. When we neglect compressibility (1) reduces to

$$\Pi V_1/RT = -\ln x_1 \,. \qquad 4.21.2$$

§4.22 *Non-ideal mixtures*

Few, if any, real mixtures are ideal, but it is convenient to correlate the thermodynamic properties of each real mixture with those of an ideal

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* McGlashan and Wingrove, Trans. Faraday Soc. 1956 **52** 470.

mixture. This is achieved most conveniently by the use of *excess functions.* For the sake of brevity we shall confine ourselves almost entirely to binary mixtures.

§4.23 *Functions of mixing and excess functions*

Consider the process of mixing an amount $1-x$ of the liquid species 1 with an amount x of the liquid species 2, at constant temperature and pressure, so as to form unit amount of a liquid mixture. The increase of G in this process is called the *proper Gibbs function of mixing* and is denoted by $\Delta_m G$. If the mixture were ideal we should have according to (4.19.3)

$$\Delta_m G^I = RT\{(1-x)\ln(1-x)+x\ln x\} \qquad 4.23.1$$

where the superscript I denotes ideal. For a real mixture we denote the excess $\Delta_m G$ over its ideal value $\Delta_m G^I$ by G_m^E and call this the *excess proper Gibbs function.* We have then

$$\begin{aligned} G_m^E/RT &= (\Delta_m G - \Delta_m G^I)/RT \\ &= (1-x)\ln\{\lambda_1/\lambda_1^0(1-x)\} + x\ln\{\lambda_2/\lambda_2^0 x\} \\ &= (1-x)\ln\{a_1/(1-x)\} + x\ln\{a_2/x\} \\ &= (1-x)\ln\{p_1/p_1^0(1-x)\} + x\ln\{p_2/p_2^0 x\}. \end{aligned} \qquad 4.23.2$$

Since there has been confusion concerning the precise meaning of (4.23.2) and related formulae, we emphasize that all the quantities λ_1, λ_2, λ_1^0, λ_2^0, a_1, a_2, p_1, p_2, p_1^0, p_2^0 relate to the same pressure P as well as the same temperature. As explained in §4.13 we measure p_1, p_2 at the total saturation pressure P_{sat} of the mixture and then calculate the values of p_1, p_2 at the chosen pressure P by means of formula (4.13.2). The chosen pressure P is usually, but not necessarily, equal to the standard pressure $P^\ominus = 1$ atm.

Other excess functions are defined similarly. It is clear that the several excess functions are interrelated in the same way as the extensive functions from which they are derived. In particular we have

$$S_m^E = -\partial G_m^E/\partial T \qquad 4.23.3$$

$$H_m^E = G_m^E - T\,\partial G_m^E/\partial T \qquad 4.23.4$$

$$V_m^E = \partial G_m^E/\partial P \qquad 4.23.5$$

$$U_m^E = G_m^E - T\,\partial G_m^E/\partial T - P\,\partial G_m^E/\partial P \qquad 4.23.6$$

$$C_m^E = -T\,\partial^2 G_m^E/\partial T^2. \qquad 4.23.7$$

Using (4.03.15) and (4.03.16) we also have

$$RT\ln\{a_1/(1-x)\}=\mu_1^{\mathrm{E}}=G_{\mathrm{m}}^{\mathrm{E}}-x\partial G_{\mathrm{m}}^{\mathrm{E}}/\partial x \qquad 4.23.8$$

$$RT\ln(a_2/x)=\mu_2^{\mathrm{E}}=G_{\mathrm{m}}^{\mathrm{E}}+(1-x)\partial G_{\mathrm{m}}^{\mathrm{E}}/\partial x. \qquad 4.23.9$$

Differentiating (2) with respect to x we obtain

$$(RT)^{-1}\,\partial G_{\mathrm{m}}^{\mathrm{E}}/\partial x=(1-x)\partial\ln p_1/\partial x+x\partial\ln p_2/\partial x+\ln\{p_1^0 p_2(1-x)/p_2^0 p_1 x\}. \qquad 4.23.10$$

By the Duhem–Margules relation we have

$$(1-x)\partial\ln p_1/\partial x+x\partial\ln p_2/\partial x=0. \qquad 4.23.11$$

Subtracting (11) from (10) we obtain

$$(RT)^{-1}\partial G_{\mathrm{m}}^{\mathrm{E}}/\partial x=\ln(p_1^0/p_2^0)+\ln\{(1-x)p_2/xp_1\}. \qquad 4.23.12$$

Integrating (12) from $x=0$ to x and observing that $G_{\mathrm{m}}^{\mathrm{E}}$ vanishes when $x=0$, we obtain

$$(RT)^{-1}G_{\mathrm{m}}^{\mathrm{E}}(x)=x\ln(p_1^0/p_2^0)+\int_0^x\ln\alpha'\,\mathrm{d}x \qquad 4.23.13$$

where α' is defined by

$$\alpha'=(1-x)p_2/xp_1. \qquad 4.23.14$$

Setting $x=1$ in (13) and remembering that $G_{\mathrm{m}}^{\mathrm{E}}$ vanishes when $x=1$ we obtain

$$\int_0^1\ln\alpha'\,\mathrm{d}x=\ln(p_2^0/p_1^0). \qquad 4.23.15$$

If then $\ln\alpha'$ is plotted against x, the two domains separated by the straight line parallel to the x-axis and distant $\ln(p_2^0/p_1^0)$ from the x-axis have equal areas.

§4.24 *Volatility ratio*

The ratio $(1-x)y/x(1-y)$, where y denotes the mole fraction of component 2 in the saturated vapour, is called the *volatility ratio* or *relative volatility* and is denoted by α. For the purpose of a rough check on the reliability of dubious measurements it is often sufficient to use the approximation of a perfect gas. To this approximation we have

$$p_1/p_2=(1-y)/y \qquad 4.24.1$$

and (4.23.14) becomes

$$\alpha'=(1-x)y/x(1-y)=\alpha. \qquad 4.24.2$$

Consequently (4.23.15) becomes

$$\int_0^1 \ln \alpha \, dx \approx \ln(P^0_{2,\mathrm{sat}}/P^0_{1,\mathrm{sat}}) \qquad 4.24.3$$

where $P^0_{1,\mathrm{sat}}$ denotes the saturated vapour pressure of pure 1 and $P^0_{2,\mathrm{sat}}$ denotes the saturated vapour pressure of pure 2. Formula (3) furnishes a rough check on the consistency of measurements of α as a function of x. We can illustrate this by using the experimental data on mixtures of water and ethanol at 25 °C given in table 4.2.

TABLE 4.2

Volatility ratio of mixtures of water and ethanol at 25 °C

x	y	α	$\ln \alpha$
0.0252	0.1790	8.421	2.131
0.0523	0.3163	8.387	2.127
0.0916	0.4334	7.582	2.026
0.1343	0.5127	6.782	1.914
0.1670	0.5448	5.969	1.787
0.2022	0.5684	5.197	1.648
0.2848	0.6104	3.935	1.370
0.3368	0.6287	3.334	1.204
0.4902	0.6791	2.201	0.789
0.5820	0.7096	1.755	0.562
0.7811	0.8161	1.244	0.218

In figure 4.6 $\ln \alpha$ is plotted against x and the straight line is at a distance $\ln(P^0_{2,\mathrm{sat}}/P^0_{1,\mathrm{sat}})$ from the x-axis. The two domains separated by this straight

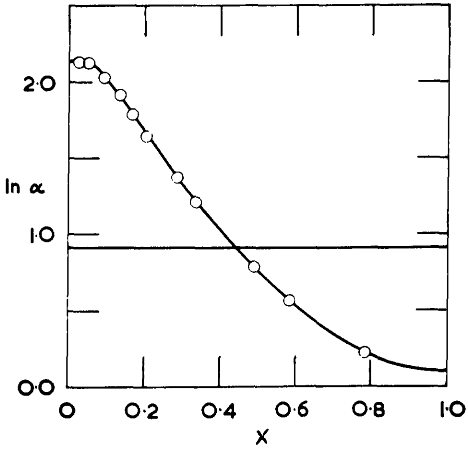

Fig. 4.6. Volatility ratio of mixtures of water and ethanol at 25 °C

line have equal areas in accordance with formula (3). This procedure for roughly checking experimental consistency was recommended independently and almost simultaneously by Redlich and Kister* and by Herington†. This kind of plot had previously been recommended by Scatchard and Raymond‡.

§4.25 *Internal stability with respect to composition*

We turn now to a discussion of internal stability with respect to composition. We can conveniently study this problem for a binary system by reference to a plot of the proper Gibbs function G_m against mole fraction x at given T, P. Examples of such plots are shown in figure 4.7.

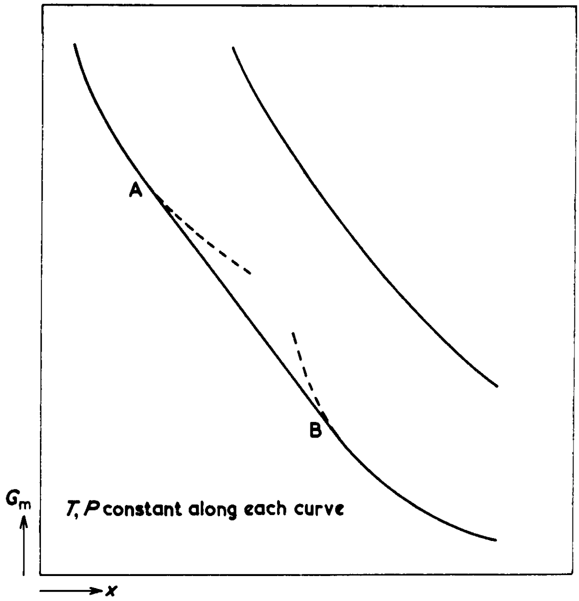

Fig. 4.7. Stable and metastable isotherms

If we now imagine a phase of composition x to split into two, one of slightly greater and the other of slightly smaller x, the new value of G_m is then given by a point on the straight line joining the two points representing the two new phases. If this point lies above the one representing the

* Redlich and Kister, Ind. Eng. Chem. 1948 **40** 345 (paper received 25 November 1946)

† Herington, Nature 1947 **160** 610 (letter dated 11 July 1947).

‡ Scatchard and Raymond, J. Amer. Chem. Soc. 1938 **60** 1281.

original phase, the system will revert to its original state which is stable. In the contrary case the original phase is unstable. It is then clear from the diagram that while the upper curve represents phases all stable, the phases represented by the dotted portion of the lower curve between A and B are metastable with respect to a mixture of phases represented by A and B.

Since according to (4.03.11)

$$\partial G_m/\partial x = G_2 - G_1 = \mu_2 - \mu_1 \qquad 4.25.1$$

we see that the slope of the curve at any point is equal to $\mu_2 - \mu_1$. Since the two phases A and B are in mutual equilibrium they have equal values of μ_1, μ_2 and consequently of $\mu_2 - \mu_1$ in agreement with the fact that the straight line AB touches the curve at A and B.

§ 4.26 *Critical mixing*

It can happen that at some temperatures the behaviour corresponds to a curve such as the upper one in figure 4.7 while at other temperatures, lower or higher, the behaviour corresponds to a curve such as the lower one. There will then be some temperature at which the change in type of behaviour takes place. This state of affairs is called *critical mixing*. At temperatures on one side of the temperature of critical mixing the two liquids are miscible in all proportions; at temperatures on the other side the miscibility is limited, only phases to the left of A or to the right of B being stable.

We shall now determine the conditions of critical mixing. The lower curve in figure 4.7 is concave upwards in the stable regions and in the dotted metastable regions. In these parts of the curve

$$\partial^2 G_m/\partial x^2 > 0. \qquad 4.26.1$$

If we imagine the two dotted curves joined into a single curve then in the middle there must be a part of the curve convex upwards corresponding to completely unstable phases. Hence between A and B there are two points of inflexion where

$$\partial^2 G_m/\partial x^2 = 0. \qquad 4.26.2$$

At the temperature of critical mixing these two points merge into a single point at which as well as (2)

$$\partial^3 G_m/\partial x^3 = 0. \qquad 4.26.3$$

Formulae (2) and (3) together express the conditions of critical mixing.

It is convenient to express these conditions of critical mixing (2) and (3) in terms of the excess proper Gibbs function G^E_m. According to the definition of G^E_m we have

$$G_m = G^E_m + (1-x)\mu^0_1 + x\mu^0_2 + RT(1-x)\ln(1-x) + RTx\ln x. \qquad 4.26.4$$

By successive differentiation with respect to x we obtain

$$\partial G_m/\partial x = \partial G^E_m/\partial x - \mu^0_1 + \mu^0_2 + RT\ln\{x/(1-x)\} \qquad 4.26.5$$

$$\partial^2 G_m/\partial x^2 = \partial^2 G^E_m/\partial x^2 + RT/x(1-x) \qquad 4.26.6$$

$$\partial^3 G_m/\partial x^3 = \partial^3 G^E_m/\partial x^3 + RT(2x-1)/x^2(1-x)^2. \qquad 4.26.7$$

Substituting (6) into (2) and (7) into (3) we obtain the conditions of critical mixing in the form

$$\partial^2 G^E_m/\partial x^2 = -RT/x(1-x) \qquad 4.26.8$$

$$\partial^3 G^E_m/\partial x^3 = -RT(2x-1)/x^2(1-x)^2. \qquad 4.26.9$$

The use of these formulae will be illustrated in §4.30.

§ 4.27 *Excess functions expressed as polynomials*

It is convenient to express the excess proper Gibbs function G^E_m of a binary mixture as a polynomial in x. We might write such a polynomial as a succession of integral powers of x but such an expression would obscure any symmetry between the two component species. Bearing in mind that G^E_m must vanish identically both when $x_1 = 1-x = 0$ and when $x_2 = x = 0$, we find it most convenient to write the polynomial in the form*

$$\begin{aligned} G^E_m &= x_1 x_2\{A_0 + A_1(x_1 - x_2) + A_2(x_1 - x_2)^2\} \\ &= x(1-x)\{A_0 + A_1(1-2x) + A_2(1-2x)^2\}. \qquad 4.27.1 \end{aligned}$$

Higher powers of $x_1 - x_2$ can be included if required. The coefficients A_0, A_1, A_2 are by definition independent of x but will usually depend on T and on P.

§ 4.28 *Symmetrical mixtures*

We shall begin by considering those mixtures for which G^E_m, and consequently G_m also, is symmetrical with respect to x_1 and x_2. Such mixtures are of interest because they correspond to the model of molecular species of the

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* Guggenheim, Trans. Faraday Soc. 1937 **33** 151 (formula 4.1); Redlich and Kister, Ind. Eng. Chem. 1948 **40** 345 (formula 8); Scatchard, Chem. Rev. 1949 **44** 9.

same size and shape. Moreover mixtures are known which conform within the experimental accuracy with formulae symmetrical in x_1 and x_2. We call such mixtures *symmetrical mixtures.*

For a symmetrical mixture $A_1=0$ and formula (4.27.1) reduces to

$$\begin{aligned} G^{\mathrm{E}}_{\mathrm{m}} &= x(1-x)\{A_0+A_2(1-2x)^2\} \\ &= (A_0+A_2)x(1-x)-4A_2x^2(1-x)^2. \end{aligned} \qquad 4.28.1$$

From (1) we derive for other excess functions

$$-S^{\mathrm{E}}_{\mathrm{m}}=x(1-x)[\partial A_0/\partial T+(\partial A_2/\partial T)(1-2x)^2] \qquad 4.28.2$$

$$H^{\mathrm{E}}_{\mathrm{m}}=x(1-x)[A_0-T(\partial A_0/\partial T)+\{A_2-T(\partial A_2/\partial T)\}(1-2x)^2] \qquad 4.28.3$$

$$V^{\mathrm{E}}_{\mathrm{m}}=x(1-x)[\partial A_0/\partial P+(\partial A_2/\partial P)(1-2x)^2] \qquad 4.28.4$$

$$\mu^{\mathrm{E}}_1=RT\ln(a_1/x_1)=x_2^2\{A_0+A_2(x_2-x_1)(x_2-5x_1)\} \qquad 4.28.5$$

$$\mu^{\mathrm{E}}_2=RT\ln(a_2/x_2)=x_1^2\{A_0+A_2(x_1-x_2)(x_1-5x_2)\}. \qquad 4.28.6$$

In (5) or (6) the term in A_2 vanishes when $x=\frac{5}{6}$ or $\frac{1}{6}$ as well as when $x=\frac{1}{2}$.

When the deviation of the vapour from a perfect gas is neglected, we obtain for the volatility ratio α using (4.23.12) and (4.24.2)

$$RT\ln(P^0_{1,\mathrm{sat}}/P^0_{2,\mathrm{sat}})+RT\ln\alpha=-(x_2-x_1)\{A_0+(1-8x_1x_2)A_2\}. \qquad 4.28.7$$

We observe that the term in A_2 vanishes when $x_1x_2=\frac{1}{8}$ as well as when $x=\frac{1}{2}$.

§ 4.29 *Simple mixtures*

We shall now consider those symmetrical mixtures for which the terms in A_2 and higher terms are negligible. Writing w in place of A_0 we have

$$G^{\mathrm{E}}_{\mathrm{m}}=x(1-x)w \qquad w=w(T,P) \qquad 4.29.1$$

where w or A_0 is independent of x but will in general depend on T and P. We call mixtures having properties defined by (1) *simple mixtures.* Such mixtures are important for several reasons.

In the first place the behaviour of these mixtures is the simplest conceivable after ideal mixtures either from a mathematical or from a physical aspect.

In the second place some binary mixtures show a behaviour which can be represented either accurately or approximately by the formulae of simple mixtures.

In the third place statistical theory predicts that a mixture of two kinds of non-polar molecules of similar simple shape and similar size should obey certain laws to which the formulae of simple mixtures are a useful approximation.

The formulae of simple mixtures, as here defined, were used by Porter* to express empirically partial vapour pressure measurements on mixtures of ethyl ether and acetone at 30 °C and a few measurements at 20 °C. The best value of w at 20 °C was found to be slightly greater than that at 30 °C. Later on Heitler† related these formulae to the model of liquids now usually called the 'quasi-crystalline' model and these formulae have been applied to experimental measurements on various mixtures especially by Hildebrand‡. It was assumed by Heitler and subsequently generally accepted that the value of w should be independent of temperature although this by no means follows from the quasi-crystalline model used in the derivation of the formulae.

From (1) we derive

$$-S_{\mathrm{m}}^{\mathrm{E}}=x(1-x)\partial w/\partial T \qquad 4.29.2$$

$$H_{\mathrm{m}}^{\mathrm{E}}=x(1-x)(w-T\partial w/\partial T) \qquad 4.29.3$$

$$V_{\mathrm{m}}^{\mathrm{E}}=x(1-x)\partial w/\partial P \qquad 4.29.4$$

$$\mu_1^{\mathrm{E}}=RT\ln\{a_1/(1-x)\}=wx^2 \qquad 4.29.5$$

$$\mu_2^{\mathrm{E}}=RT\ln\{a_2/x\}=w(1-x)^2. \qquad 4.29.6$$

We shall now compare the formulae of simple mixtures with the experimental data on mixtures of carbon tetrachloride and cyclohexane. For these mixtures $G_{\mathrm{m}}^{\mathrm{E}}$ has been determined by vapour pressure measurements at 30, 40, 50, 60, and 70 °C. There are also measurements of the enthalpy of mixing $\Delta_{\mathrm{m}}H$ at 10, 25, 40, and 55 °C. The experimental values§ of $G_{\mathrm{m}}^{\mathrm{E}}$ are shown plotted against $x(1-x)$ in figure 4.8. According to formula (1) the slopes of the straight lines are the values of w at each temperature. The experimental values‖ of $H_{\mathrm{m}}^{\mathrm{E}}=\Delta_{\mathrm{m}}H$ are shown similarly plotted in figure 4.9. According to formula (3) the slopes of the straight lines are the values of $w-T(\partial w/\partial T)$ at each temperature. The fact that the experimental points for $x<\frac{1}{2}$ shown to the left and those for $x>\frac{1}{2}$ shown to the right lie on the pair of straight lines confirms that the laws of simple mixtures are valid within the experimental accuracy. The thermodynamic consistency of the two sets of data requires that both should be fitted by the same values of w and

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* Porter, Trans. Faraday Soc. 1920 **16** 336.

† Heitler, Ann. Phys., Lpz. 1926 **80** 629.

‡ Hildebrand and Scott, Solubility of Nonelectrolytes, Reinhold 1950.

§ Scatchard, Wood and Mochel, J. Amer. Chem. Soc. 1939 **61** 3206; Brown and Ewald, Australian J. Sci. Res. A 1950 **3** 306.

‖ Adcock and McGlashan, Proc. Roy. Soc. A 1954 **226** 266.

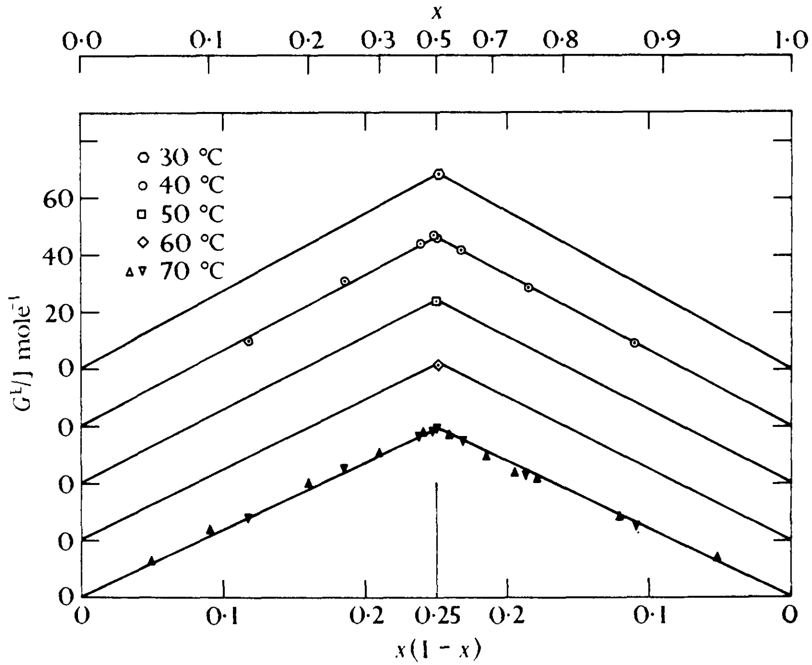

Fig. 4.8. Excess Gibbs function in mixtures of carbon tetrachloride and cyclohexane

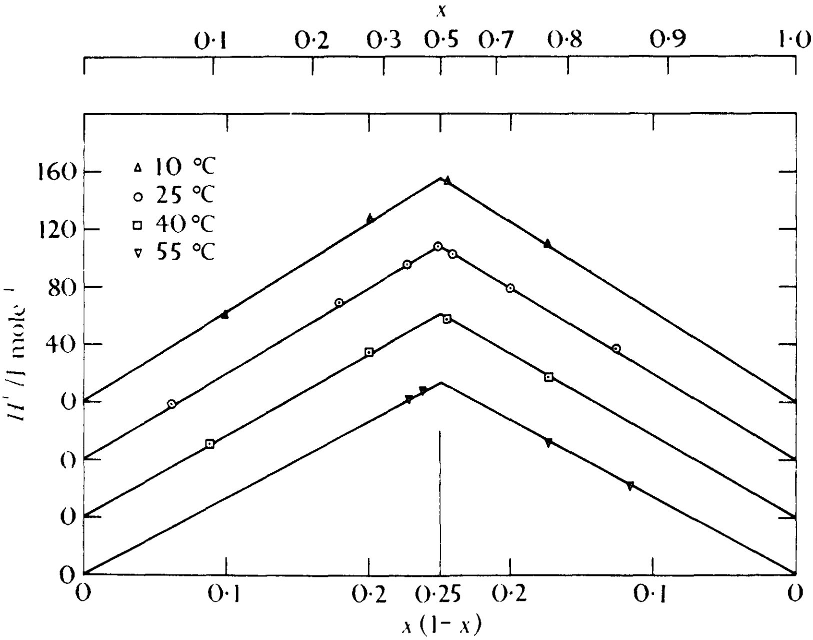

Fig. 4.9. Enthalpy of mixing in mixtures of carbon tetrachloride and cyclohexane

$\partial w/\partial T$. The straight lines in both figure 4.8 and figure 4.9 in fact correspond to the single relation*

$$w/\text{J mole}^{-1} = 1176 + 1.96T \ln T - 14.18T \qquad 4.29.7$$

so that

$$(w - T\partial w/\partial T)/\text{J mole}^{-1} = 1176 - 1.96T. \qquad 4.29.8$$

§ 4.30 *Critical mixing in simple mixtures*

In figure 4.10 the quantities $a_1 = p_1/p_1^0$ and $a_2 = p_2/p_2^0$ are plotted against x for simple mixtures with $w/RT = 1$ and $w/RT = -2$. When w is positive, the curves lie above the straight lines representing the behaviour of an ideal mixture; this situation is called a *positive deviation* from ideality. On the other hand when w is negative, both curves lie below the straight line of the ideal mixture and this situation is described as a *negative deviation* from ideality.

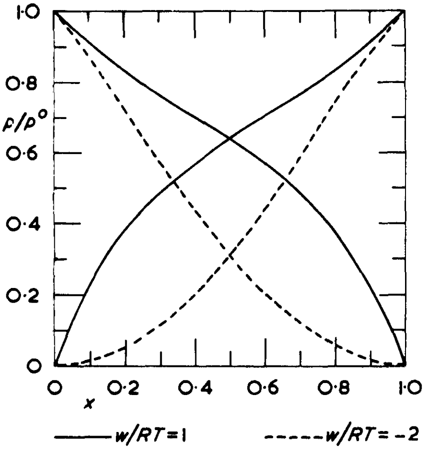

Fig. 4.10. Relative activities of simple mixtures: (complete mixing)

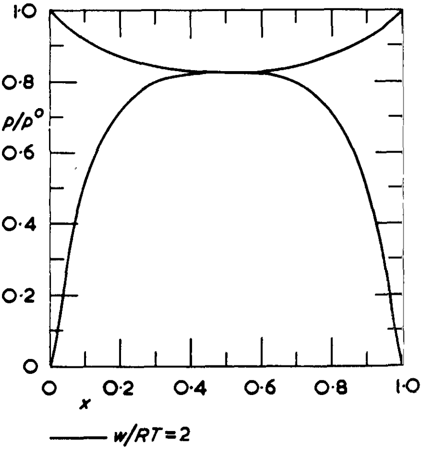

Fig. 4.11. Relative activities of simple mixture: (temperature of critical mixing)

Figure 4.11 gives similar plots for $w/RT = 2$. We shall now show that this determines the temperature of critical mixing. We begin by recalling the general conditions for critical mixing (4.26.8) and (4.26.9)

$$\partial^2 G_m^E/\partial x^2 = -RT/x(1-x) \qquad 4.30.1$$

$$\partial^3 G_m^E/\partial x^3 = -RT(2x-1)/x^2(1-x)^2. \qquad 4.30.2$$

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* Adcock and McGlashan, Proc. Roy. Soc. A 1954 **226** 266.

We also recall formula (4.29.1) which defines simple mixtures

$$G_{\mathrm{m}}^{\mathrm{E}}=x(1-x)w \qquad w=w(T, P). \tag{4.30.3}$$

By successive differentiation of (3) with respect to x we obtain

$$\partial G_{\mathrm{m}}^{\mathrm{E}}/\partial x=(1-2x)w \tag{4.30.4}$$

$$\partial^2 G_{\mathrm{m}}^{\mathrm{E}}/\partial x^2=-2w \tag{4.30.5}$$

$$\partial^3 G_{\mathrm{m}}^{\mathrm{E}}/\partial x^3=0. \tag{4.30.6}$$

By substituting (5) into (1) and (6) into (2) we obtain as the conditions for critical mixing in a simple mixture

$$-2w=-RT/x(1-x) \tag{4.30.7}$$

$$0=RT(2x-1)/x^2(1-x)^2. \tag{4.30.8}$$

From (8) we deduce $x=\frac{1}{2}$, which is incidentally obvious from considerations of symmetry, and substituting this value of x into (7) we obtain for the temperature T_{c} of critical mixing

$$2RT_{\mathrm{c}}=w \tag{4.30.9}$$

in agreement with figure 4.11.

When $w/RT>2$ there is incomplete mixing. A typical example, namely $w/RT=3$, is shown in figure 4.12. If x', x'' denote the compositions of the two phases in mutual equilibrium at a given temperature below that of critical mixing, then x', x'' are determined by the pair of simultaneous equations

$$p_1(x')=p_1(x'') \tag{4.30.10}$$

$$p_2(x')=p_2(x''). \tag{4.30.11}$$

Dividing (10) by p_1^0 and dividing (11) by p_2^0 we obtain the equivalent pair of simultaneous equations

$$a_1(x')=a_1(x'') \tag{4.30.12}$$

$$a_2(x')=a_2(x''). \tag{4.30.13}$$

The conditions (12) and (13) hold for the two-phase equilibrium of any binary mixture. In the particular case of simple mixtures there is complete symmetry between a_1 as a function of x and a_2 as a function of $1-x$. It follows from this symmetry that

$$x'+x''=1 \tag{4.30.14}$$

and consequently (12) and (13) lead to

$$a_1(x') = a_1(x'') = a_2(1 - x'') = a_2(x'). \qquad 4.30.15$$

Hence x', x'' are determined by the intersections of the two curves. These are the points L, M in figure 4.12. The curves between L and M represent solutions either metastable near L, M or completely unstable towards the middle of the diagram.

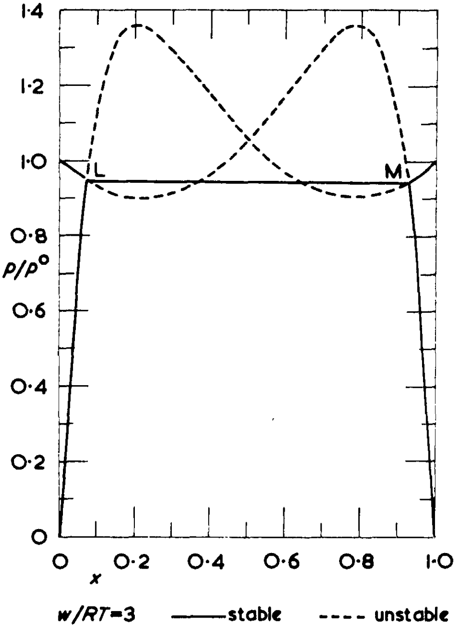

Fig. 4.12. Relative activities of simple mixture: (incomplete mixing)

When we substitute from (4.29.5) and (4.29.6) into (15) we obtain as the equation for either x' or x''

$$(1 - x)/x = \exp\{(1 - 2x)w/RT\}. \qquad 4.30.16$$

If we use the abbreviation $s = 1 - 2x$ we can rewrite (16) as an equation for s in the form

$$s = \tanh(sw/2RT) \qquad 4.30.17$$

which can be solved numerically by inspection of tables of the tanh function. Incidentally we notice from (17) that $s \to 0$ as $w/2RT \to 1$, that is to say at critical mixing.

Pairs of liquids are known, for example water and nicotine, which are completely miscible above a certain critical temperature and below another critical temperature, but are incompletely miscible in the intermediate temperature range. It is interesting to note that even simple mixtures can behave in this way when w is a quadratic function of the temperature provided the three coefficients in the quadratic expression have suitable signs and magnitudes. To be precise if w has the quadratic form*

$$w/R=2T+\{t^2-(T-T_0)^2\}/\Theta \qquad 4.30.18$$

where Θ, T_0, and t are positive constants and $t<T_0$, then it is clear that $w/R=2T$ when $T=T_0-t$ or $T=T_0+t$. It can also be verified that $w/R>2T$ when $T_0-t<T<T_0+t$ and that $w/R<2T$ when $T>T_0+t$ or $T<T_0-t$. Consequently the temperature range of incomplete miscibility extends from T_0-t to T_0+t.

Incidentally the converse behaviour occurs, that is complete miscibility only between the two critical temperatures, if Θ is negative.

§ 4.31 *Critical mixing in symmetrical mixtures*

We shall now consider briefly the condition for critical mixing in a symmetrical mixture which is not a simple mixture. If we assume

$$G^{\mathrm{E}}_{\mathrm{m}}=x(1-x)\{A_0+A_2(1-2x)^2+A_4(1-2x)^4\} \qquad 4.31.1$$

then it is obvious from symmetry that at the critical point $x=\frac{1}{2}$. For this value of x

$$\partial^2 G^{\mathrm{E}}_{\mathrm{m}}/\partial x^2=-2(A_0-A_2). \qquad 4.31.2$$

Consequently by (4.26.8)

$$-2(A_0-A_2)=-4RT \qquad 4.31.3$$

or

$$(A_0-A_2)/RT=2. \qquad 4.31.4$$

It is interesting to note that this condition is independent of A_4, and incidentally also of coefficients of higher powers of $(1-2x)^2$.

§ 4.32 *Example of unsymmetrical mixture*

By way of contrast with symmetrical mixtures we shall now briefly illustrate the opposite type of behaviour by a particular hypothetical example. We return to formula (4.27.1). Instead of setting $A_1=0$ and so obtaining

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* Guggenheim, Faraday Soc. Discussion No. 15 1953 271.

the formulae of symmetrical mixtures, we now set $A_0+A_1=0$ and $A_2=0$. We then obtain

$$G_m^E=Ax^2(1-x) \qquad 4.32.1$$

where we have written A instead of $2A_0$.

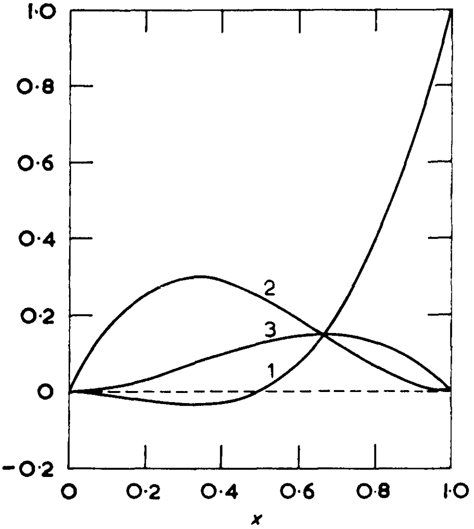

Fig. 4.13. Example of unsymmetrical excess functions
Curve 1 $(RT/A)\ln\{a_1/(1-x)\}$
Curve 2 $(RT/A)\ln\{a_2/x\}$
Curve 3 G_m^E/A

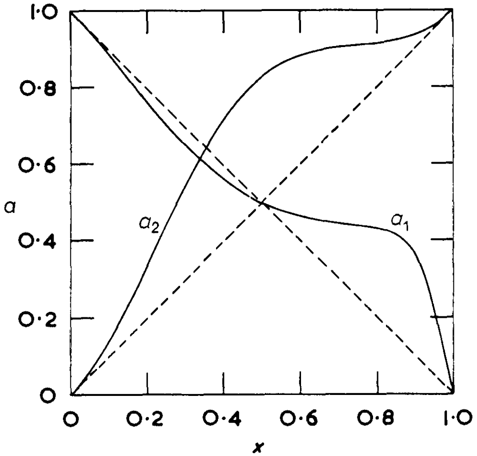

Fig. 4.14. Example of relative activities in a mixture having unsymmetrical excess functions

From (1) we obtain, using (4.23.8) and (4.23.9)

$$RT\ln\{a_1/(1-x)\}=Ax^2(2x-1) \qquad 4.32.2$$

$$RT\ln\{a_2/x\} \qquad =2Ax(1-x)^2. \qquad 4.32.3$$

A remarkable feature* of this pair of formulae is that, whereas $\ln\{a_2/x\}$ has for all values of x the same sign as A, the sign of $\ln\{a_1/(1-x)\}$ changes at $x=\frac{1}{2}$. This behaviour with $A=\frac{1}{2}RT$ is illustrated in figure 4.14.

§4.33 *Athermal mixtures of small and large molecules*

According to (4.19.12) when two or more species form an ideal mixture, then they mix isothermally without increase or decrease of the enthalpy. Zero enthalpy of mixing is thus a necessary condition for two or more species to form an ideal mixture, but it is not a sufficient condition. Mixtures, not necessarily ideal, having zero enthalpy of mixing at all compositions are called *athermal mixtures*. Statistical mechanics indicates as a further necessary condition for a mixture to be ideal that the several kinds of molecules should not differ greatly in size. It is accordingly of interest to consider the properties of mixtures of two kinds of molecules sufficiently similar to mix in all proportions without any enthalpy of mixing, but differing widely in size. This is a complicated problem in statistical mechanics which has not been solved completely. It is probable that the shapes of the molecules matter as well as their sizes. However, when we ignore such complications, there are reasons for believing that the behaviour due to wide differences in size between the two species of molecule can be at least semi-quantitatively described by means of relatively simple formulae in which the only new parameter is the ratio of the molecular volumes.

If ϱ denotes the ratio of the volume of a molecule of type 2 to that of a molecule of type 1, then subject to various restrictions and approximations which we shall not here go into, we may write for the proper Gibbs function of mixing†

$$\Delta_{\mathrm{m}}G=RT(1-x)\ln\{(1-x)/(1-x+\varrho x)\}+RTx\ln\{\varrho x/(1-x+\varrho x)\}. \qquad 4.33.1$$

Formula (1) is more easily memorized if written in a slightly different form involving the *volume fraction* ϕ of the second species defined by

$$\phi \;=\; \varrho x/(1-x+\varrho x). \qquad 4.33.2$$

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* McGlashan, J. Chem. Ed. 1963 **40** 516.

† Guggenheim, Mixtures, Clarendon Press 1952.

Using (2) we can rewrite (1) in the shorter form

$$\Delta_m G = RT(1-x)\ln(1-\phi) + RTx\ln\phi. \qquad 4.33.3$$

This simple formula is due to Flory.*

From (3) we deduce using (4.03.15) and (4.03.16)

$$\begin{aligned}\ln a_1 &= \ln(p_1/p_1^0) = \ln(\lambda_1/\lambda_1^0) = \ln\{(1-x)/(1-x+\varrho x)\} + (\varrho-1)x/(1-x+\varrho x)\\ &= \ln(1-\phi) + (1-\varrho^{-1})\phi \qquad 4.33.4\end{aligned}$$

$$\begin{aligned}\ln a_2 &= \ln(p_2/p_2^0) = \ln(\lambda_2/\lambda_2^0) = \ln\{\varrho x/(1-x+\varrho x)\} - (\varrho-1)(1-x)/(1-x+\varrho x)\\ &= \ln\phi - (\varrho-1)(1-\phi). \qquad 4.33.5\end{aligned}$$

We notice that when $\varrho=1$ we recover the formulae of ideal mixtures. Of especial interest is the opposite extreme when ϱ is so great that $1/\varrho$ may be neglected compared with unity. Formula (4) then reduces to

$$\ln a_1 = \ln(p_1/p_1^0) = \ln(\lambda_1/\lambda_1^0) = \ln(1-\phi) + \phi \qquad (\varrho\to\infty). \qquad 4.33.6$$

We then have the remarkable situation that the lowering of the vapour pressure of the 'solvent' species 1 is completely determined by the volume fraction of the 'solute' species 2. Under these conditions determinations of the vapour pressure of the solvent give no information concerning the size of the solute molecules, except that they are much larger than the solvent molecules. These formulae are relevant to solutions of rubber or polystyrene in certain non-polar solvents such as benzene and toluene.

§ 4.34 *Osmotic pressure in athermal mixtures*

By substituting (4.33.4) into (4.14.10) we obtain for the osmotic pressure with respect to a membrane permeable only to the species 1 with small molecules

$$\Pi\langle V_1\rangle/RT = -\ln(1-\phi) - (1-\varrho^{-1})\phi. \qquad 4.34.1$$

If we expand $\ln(1-\phi)$ in powers of ϕ we obtain

$$\Pi\langle V_1\rangle/RT = \phi/\varrho + \tfrac{1}{2}\phi^2 + \tfrac{1}{3}\phi^3 + \dots. \qquad 4.34.2$$

From (2) and (4.33.2) we see that in the limit of infinite dilution $\Pi \propto x$ as usual, but for this state of affairs it is not sufficient that $\phi \ll 1$, the much more stringent condition $\varrho\phi \ll 1$ being required. If we merely assume that $\phi \ll 1$ formula (2) reduces to

$$\Pi\langle V_1\rangle/RT = \phi/\varrho + \tfrac{1}{2}\phi^2 \qquad (\phi \ll 1) \qquad 4.34.3$$

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* Flory, J. Chem. Phys. 1941 **9** 660; 1942 **10** 51.

and the term $\frac{1}{2}\phi^2$ will swamp the term ϕ/ϱ unless $\phi \ll \varrho^{-1}$. It follows from this that in a solution of macromolecules measurements of osmotic pressure cannot yield simple or reliable information concerning the size of the solute macromolecules unless the solutions are so dilute that $\phi \ll \varrho^{-1}$ which implies that $x \ll \varrho^{-2}$.

§4.35 *Interfacial layers*

We shall now consider the thermodynamics of interfacial layers between two bulk phases each containing the same two components. There are two cases to distinguish: first an interface between a liquid mixture and its vapour, when the interfacial tension is called the *surface tension*; second an interface between two liquid layers containing in different proportions two incompletely miscible components.

We shall first discuss the liquid–vapour interface using an approximation sufficient for most if not all practical applications. We shall next give a similar approximate treatment of a liquid–liquid interface. Finally we shall give an accurate treatment applicable in principle to either type of interface, but of small practical use.

§4.36 *Liquid–vapour interface*

We begin with formula (1.57.3) applied to a system of two components 1 and 2. Thus

$$-\mathrm{d}\gamma = S^{\sigma}_{A}\mathrm{d}T - \tau\mathrm{d}P + \Gamma_1\mathrm{d}\mu_1 + \Gamma_2\mathrm{d}\mu_2\,. \qquad 4.36.1$$

In the liquid phase we have according to (4.04.4) and (4.04.6)

$$\mathrm{d}\mu_1 = -S_1\mathrm{d}T + V_1\mathrm{d}P + (\partial\mu_1/\partial x)\mathrm{d}x \qquad 4.36.2$$

$$\mathrm{d}\mu_2 = -S_2\mathrm{d}T + V_2\mathrm{d}P + (\partial\mu_2/\partial x)\mathrm{d}x \qquad 4.36.3$$

where we have omitted superscripts from quantities relating to the liquid phase.

In our initial treatment of a liquid–vapour interface we shall make approximations similar to those used in §3.63 for a single-component interface.

In the first place we assume that in the liquid phase PV_1 and PV_2 are so small compared with RT that they may be neglected.

In the second place we assume that the two geometrical surfaces separating the interfacial phase from the two bulk phases are placed so near to each other that terms in $P\tau$ may also be neglected. We accordingly replace (1), (2), (3) by

$$-\mathrm{d}\gamma = S^\sigma_A \mathrm{d}T + \Gamma_1 \mathrm{d}\mu_1 + \Gamma_2 \mathrm{d}\mu_2 \qquad 4.36.4$$

$$\mathrm{d}\mu_1 = -S_1 \mathrm{d}T + (\partial\mu_1/\partial x)\mathrm{d}x \qquad 4.36.5$$

$$\mathrm{d}\mu_2 = -S_2 \mathrm{d}T + (\partial\mu_2/\partial x)\mathrm{d}x. \qquad 4.36.6$$

Substituting (5) and (6) into (4) we obtain

$$-\mathrm{d}\gamma = (S^\sigma_A - \Gamma_1 S_1 - \Gamma_2 S_2)\mathrm{d}T + \{\Gamma_1(\partial\mu_1/\partial x) + \Gamma_2(\partial\mu_2/\partial x)\}\mathrm{d}x. \qquad 4.36.7$$

The system of two components in liquid and vapour has two degrees of freedom. There are consequently two independent variables, for which we choose T and x. Formula (7) thus expresses variations of the surface tension γ in terms of variations $\mathrm{d}T$ and $\mathrm{d}x$ of the two independent variables.

Since the quantities $\partial\mu_1/\partial x$ and $\partial\mu_2/\partial x$ on the right of (7) are related by the Gibbs–Duhem relation

$$(1-x)\partial\mu_1/\partial x + x(\partial\mu_2/\partial x) = 0 \qquad (T, P \text{ const.}) \qquad 4.36.8$$

we can use this relation to eliminate either of them. If for example we eliminate $\partial\mu_1/\partial x$ we obtain

$$-\mathrm{d}\gamma = (S^\sigma_A - \Gamma_1 S_1 - \Gamma_2 S_2)\mathrm{d}T + \{\Gamma_2 - x\Gamma_1/(1-x)\}(\partial\mu_2/\partial x)\mathrm{d}x. \qquad 4.36.9$$

By this elimination we have unavoidably destroyed the symmetry between the components 1 and 2.

§ 4.37 *Invariance of relations*

We recall that according to the definition in § 1.53 of a surface phase the properties associated with it depend on the positions of the boundaries AA′ and BB′ in figure 1.2. As in § 3.62 we shall henceforth refer to the boundary between surface layer and liquid as Lσ and that between surface layer and gas as Gσ. Since the precise positions assigned to these geometrical boundaries are partly arbitrary, the values assigned to such quantities as Γ_1, Γ_2, S^σ are also arbitrary. We can nevertheless verify that our formulae are invariant with respect to shifts of either or both of these boundaries. It is hardly necessary to mention that the intensive variables T, μ_1, μ_2 are unaffected by shifts of either boundary. It is also clear from the definition of γ in § 1.54 that its value is invariant.

Let us now consider a shift of the plane boundary Lσ a distance $\delta\tau$ away from the gas phase. Then Γ_1 becomes increased by the amount of the species 1 in a cylinder of liquid of height $\delta\tau$, of cross-section unity and so of volume $\delta\tau$. But the total amount of substance in the volume $\delta\tau$ is $\delta\tau/V_\mathrm{m}$ of which the amount of species 1 is $(1-x)\delta\tau/V_\mathrm{m}$. Similarly Γ_2 becomes increased by $x\delta\tau/V_{\mathrm{m}}$. Consequently although shifting the boundary Lσ alters the values of Γ_1 and Γ_2, the quantity

$$\Gamma_2 - x\Gamma_1/(1-x) \qquad 4.37.1$$

remains unchanged. The invariant quantity (1) is essentially the same as a quantity defined by Gibbs in a more abstract manner which he denoted by the symbol $\Gamma_{2(1)}$.

Similarly when the boundary Lσ is shifted a distance $\delta\tau$ away from the gas phase, S^{σ} becomes increased by the entropy contained in a cylinder of liquid of volume $\delta\tau$, that is to say by an amount

$$S_{\mathrm{m}}\delta\tau/V_{\mathrm{m}} = \{(1-x)S_1 + xS_2\}\delta\tau/V_{\mathrm{m}}. \qquad 4.37.2$$

At the same time $\Gamma_1 S_1$ is increased by $S_1(1-x)\delta\tau/V_{\mathrm{m}}$ and $\Gamma_2 S_2$ by $S_2 x\delta\tau/V_{\mathrm{m}}$. Consequently the quantity

$$S^{\sigma}_{A} - \Gamma_1 S_1 - \Gamma_2 S_2 \qquad 4.37.3$$

occurring in (4.36.9) remains invariant.

With regard to a shift of the geometrical surface Gσ, little need be said in the present connection. For our approximation of neglecting terms in $P\tau$, as we are doing, is equivalent to assuming that the amount of substance per unit volume in the gas phase is negligible compared with that in unit volume of the surface layer. Consequently if we shifted the geometrical surface Gσ away from the liquid even to the extent of doubling the value of τ, the change in the amount of substance contained in the surface layer would be negligible and consequently the values of Γ_1, Γ_2, S^{σ}_{A} would not be appreciably affected.

§ 4.38 *Temperature coefficient of surface tension*

If we apply formula (4.36.9) to variations of temperature at constant composition x of the liquid we obtain

$$-\mathrm{d}\gamma/\mathrm{d}T = S^{\sigma}_{A} - \Gamma_1 S_1 - \Gamma_2 S_2 \qquad (\text{const. } x). \qquad 4.38.1$$

This relation involving entropies can be transformed to one involving energies as follows. Since we are neglecting terms in PV_1 and PV_2 we may replace (4.04.3) by the approximation

$$\mu_1 = \textit{Æ}_1 = U_1 - TS_1 \qquad 4.38.2$$

$$\mu_2 = \textit{Æ}_2 = U_2 - TS_2. \qquad 4.38.3$$

Applying formula (1.56.1) to unit area and neglecting the term containing

$V^\sigma = \tau A$, we have

$$\Gamma_1 \mu_1 + \Gamma_2 \mu_2 = U_A^\sigma - TS_A^\sigma - \gamma. \qquad 4.38.4$$

We now use (2), (3), (4) to eliminate S_A^σ, S_1, S_2 from (1). We thus obtain

$$\gamma - T\mathrm{d}\gamma/\mathrm{d}T = U_A^\sigma - \Gamma_1 U_1 - \Gamma_2 U_2. \qquad 4.38.5$$

It is worth noticing that the right side of (1) is the entropy of unit area of interface less the entropy of the same material content in the liquid phase. Likewise the right side of (5) is the energy of unit area of interface less the energy of the same material content in the liquid phase. More pictorially we may say that it is the energy which must be supplied to prevent any change of temperature when unit area of surface is formed from the liquid. It may appropriately be called the *surface energy* of formation of unit area.

§ 4.39 *Variations of composition*

If we apply (4.36.7) to a variation of composition at constant temperature we obtain, using (4.12.7),

$$\begin{aligned} -\partial\gamma/\partial x &= \Gamma_1 \partial\mu_1/\partial x + \Gamma_2 \partial\mu_2/\partial x \\ &= RT(\Gamma_1 \partial \ln \lambda_1/\partial x + \Gamma_2 \partial \ln \lambda_2/\partial x) \\ &= RT(\Gamma_1 \partial \ln a_1/\partial x + \Gamma_2 \partial \ln a_2/\partial x) \\ &= RT(\Gamma_1 \partial \ln p_1/\partial x + \Gamma_2 \partial \ln p_2/\partial x) \qquad (T \text{ const.}). \end{aligned} \qquad 4.39.1$$

When we combine (1) with the Gibbs–Duhem relation (4.16.1) or with the Duhem–Margules relation (4.16.4) we obtain

$$\begin{aligned} -\partial\gamma/\partial x &= -RT\{(1-x)\Gamma_2 - x\Gamma_1\}x^{-1} \partial \ln \lambda_1/\partial x \\ &= RT\{(1-x)\Gamma_2 - x\Gamma_1\}(1-x)^{-1} \partial \ln \lambda_2/\partial x \end{aligned} \qquad 4.39.2$$

or alternatively

$$\begin{aligned} -\partial\gamma/\partial x &= -RT\{(1-x)\Gamma_2 - x\Gamma_1\}x^{-1} \partial \ln p_1/\partial x \\ &= RT\{(1-x)\Gamma_2 - x\Gamma_1\}(1-x)^{-1} \partial \ln p_2/\partial x. \end{aligned} \qquad 4.39.3$$

From (3) we see that from measurements of γ and p_1 or p_2 over a range of compositions we can for each composition compute the value of the quantity I defined by

$$I = (1-x)\Gamma_2 - x\Gamma_1. \qquad 4.39.4$$

We have already verified in §4.37 that $I/(1-x)$ is invariant with respect to shift in position of the boundary Lσ between the liquid and the interface.

Obviously the same holds for I itself. Values can be assigned to Γ_1 and Γ_2 individually only by adopting some more or less arbitrary convention.* We shall illustrate this by a numerical example in the next section. Since Γ_1, Γ_2 must be finite, it follows from (4) that

$$\Gamma_2/I \to 1 \quad \text{as} \quad x \to 0 \tag{4.39.5}$$

$$-\Gamma_1/I \to 1 \quad \text{as} \quad x \to 1. \tag{4.39.6}$$

This implies that for small values of x the value of Γ_2 is unaffected by the position assigned to the boundary Lσ and that for small values of $1-x$ the value of Γ_1 is unaffected. Consequently when $x \ll 1$ we may regard I as a measure of the positive adsorption Γ_2 of species 2 at the surface and when $1-x \ll 1$ we may regard $-I$ as a measure of the adsorption Γ_1 of the species 1. At intermediate values of x no such simple physical meaning can be attached to I. We may however regard I as a measure of relative adsorption of the two species.

In the special case of an ideal mixture formula (3) becomes

$$-(RT)^{-1}\partial\gamma/\partial x = \Gamma_2/x - \Gamma_1/(1-x) = I/x(1-x). \tag{4.39.7}$$

§4.40 *Example of water + ethanol*

We shall now consider the experimental data for mixtures of water and ethanol in order to illustrate the use of the formulae of the preceding section. We neglect the difference between fugacity and partial pressure. The experimental data for the partial vapour pressures have already been given in figure 4.3 and table 4.1 where we verified that they are consistent with the Duhem–Margules relation. In table 4.3 the first three columns repeat those of table 4.1, the subscripts $_1$ denoting water and $_2$ ethanol. The fourth column gives experimental values of the surface tension γ. The fifth column gives values of $-\partial\gamma/\partial \ln p_2$ obtained by plotting γ against $\ln p_2$ and measuring slopes. The sixth column gives values of

$$I = (1-x)\Gamma_2 - x\Gamma_1 \tag{4.40.1}$$

calculated from (4.39.3) which can be rewritten in the form

$$-\partial\gamma/\partial \ln p_2 = RTI/(1-x). \tag{4.40.2}$$

The values of I are given in the sixth column. In the seventh column the corresponding molecular quantity I/L is given.

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* Guggenheim and Adam, Proc. Roy. Soc. A 1933 **139** 231.

TABLE 4.3

Mixtures of water and ethanol at 25 °C
Determination of $I=(1-x)\Gamma_2-x\Gamma_1$

x	p_1 / mmHg	p_2 / mmHg	γ / erg cm^{-2}	$-\partial\gamma/\partial \ln p_2$ / erg cm^{-2}	$10^{10}I$ / mole cm^{-2}	$10^2 I/L$ / Å^{-2}
0.0	23.75	0.0	72.2	0.0	0.0	0.0
0.1	21.7	17.8	36.4	15.6	5.6	9.3
0.2	20.4	26.8	29.7	16.0	5.1	8.5
0.3	19.4	31.2	27.6	14.6	4.1	6.8
0.4	18.35	34.2	26.35	12.6	3.0	5.0
0.5	17.3	36.9	25.4	10.5	2.1	3.5
0.6	15.8	40.1	24.6	8.45	1.4	2.3
0.7	13.3	43.9	23.85	7.15	0.8	1.3
0.8	10.0	48.3	23.2	6.2	0.5	0.8
0.9	5.5	53.3	22.6	5.45	0.2	0.3
1.0	0.0	59.0	22.0	5.2	0.0	0.0

As we have repeatedly emphasized, this is as far as one can go without using some non-thermodynamic convention. We shall now give an example of such a convention*. Let us assume that the interfacial layer is unimolecular and that each molecule of water occupies a constant area of interface and likewise each molecule of ethanol. This assumption may be expressed by

$$A_1\Gamma_1+A_2\Gamma_2=1 \qquad (A_1, A_2 \text{ const.}). \tag{4.40.3}$$

We may call A_1, A_2 the *partial areas* of the two species in the interface. The essence of our assumption is not the definition of these quantities, but the assignment to them of definite constant values which can neither be determined nor be verified by thermodynamic means.

As an example we might assume

$$\begin{aligned} A_1 &= 0.04\times10^{10}\ \text{cm}^2\ \text{mole}^{-1} \\ A_2 &= 0.12\times10^{10}\ \text{cm}^2\ \text{mole}^{-1} \end{aligned} \tag{4.40.4}$$

corresponding to molecular cross-sections

$$\begin{aligned} A_1/L &= 7\ \text{Å}^2 \\ A_2/L &= 20\ \text{Å}^2. \end{aligned} \tag{4.40.5}$$

The relation (3) with the values of A_1, A_2 given by (4) is sufficient to determine values of Γ_1, Γ_2 from the values of the expression (1) already given in table 4.3. The results of the calculation are given in table 4.4.

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* Guggenheim and Adam, Proc. Roy. Soc. A 1933 **139** 231.

TABLE 4.4

Mixtures of water and ethanol at 25 °C

Values of Γ_1 and Γ_2 calculated from $A_1\Gamma_1+A_2\Gamma_2=1$

with $A_1=0.04\times10^{10}$ cm² mole⁻¹ of water

$A_2=0.12\times10^{10}$ cm² mole⁻¹ of ethanol

x	$\frac{10^{10}I}{\text{mole cm}^{-2}}$	$\frac{10^{10}\Gamma_2}{\text{mole cm}^{-2}}$	$\frac{10^{10}\Gamma_1}{\text{mole cm}^{-2}}$	$\frac{\Gamma_2}{\Gamma_1+\Gamma_2}$
0.0	0.0	0.0	25.0	0.00
0.1	5.6	6.8	4.6	0.60
0.2	5.1	7.25	3.25	0.69
0.3	4.1	7.25	3.25	0.69
0.4	3.0	7.25	3.25	0.69
0.5	2.1	7.3	3.1	0.70
0.6	1.4	7.45	2.65	0.74
0.7	0.8	7.65	2.0	0.79
0.8	0.5	7.9	1.3	0.86
0.9	0.2	8.1	0.7	0.94
1.0	0.0	8.35	0.0	1.00

The first column gives the mole fraction x of ethanol, the second the values of I taken from the previous table, the third and fourth columns the values of Γ_1, Γ_2 calculated by means of (3). The fifth column gives the values of $\Gamma_2/(\Gamma_1+\Gamma_2)$ which we may call the *mole fraction* of ethanol *in the surface layer.* As the mole fraction, thus calculated, in the surface layer increases steadily with the mole fraction in the liquid, we may conclude that although the model on which the assumptions (3), (4), (5) were based is admittedly arbitrary, at least it does not lead to unreasonable or surprising results.

§ 4.41 *Interface between two binary liquids*

We turn now to consider the interface between two liquid phases of two components 1 and 2. Two such phases may or may not be simple, but they obviously cannot be ideal. In our initial treatment we shall make approximations similar to those in §4.36.

We assume that in a liquid phase PV_1 and PV_2 are so small compared with RT that they may be neglected. This assumption now applies to both liquid phases. Just as in §4.36 we also neglect terms in $P\tau$.

There is an important physical difference between the significance of our approximate treatment of a liquid–vapour interface in the previous sections and the approximate treatment we are now about to give of a liquid–liquid interface. In the case of the liquid–vapour system we took as independent variables the temperature and composition of the liquid phase. Since the system has two degrees of freedom, these determine the composition and pressure of the vapour phase. Moreover the consequent variations of pressure are significant in determining the thermodynamic properties of the vapour phase. In our present discussion of a liquid–liquid system we are assuming that the thermodynamic properties of all phases, that is both liquids and interface, are independent of the pressure. We are thus effectively suppressing variability of pressure as a possible degree of freedom. But when we do this, a single binary liquid phase has only two remaining degrees of freedom, so that we might take as variables either T, x which are independent or T, μ_1, μ_2 subject to the Gibbs–Duhem relation. Correspondingly in a system of two binary liquid phases the variables T, μ_1, μ_2 are subject to two Gibbs–Duhem relations, one in each phase. Thus the system has effectively only one degree of freedom instead of two. Hence the temperature completely determines the composition of both liquid phases and so also the properties of the interface.

We may alternatively describe the situation as follows. A binary liquid–liquid system, like a binary liquid–vapour system has two degrees of freedom. We may therefore take as independent variables T, P and these will then determine the composition of both phases and so also the properties of the interface. When however we use the approximation of treating the properties of every phase as effectively independent of P, then clearly all the equilibrium properties are completely determined by T.

We accordingly proceed to determine how the interfacial tension depends on the temperature.

§4.42 *Temperature dependence of interfacial tension*

We begin with formula (4.36.4)

$$-\mathrm{d}\gamma = S^{\sigma}_{A}\mathrm{d}T + \Gamma_1\mathrm{d}\mu_1 + \Gamma_2\mathrm{d}\mu_2 \qquad 4.42.1$$

which applies as well to a liquid–liquid as to a liquid–vapour interface. We also have a Gibbs–Duhem relation in each of the liquid phases. With the term $V_{\mathrm{m}}\mathrm{d}P$ neglected, we have, denoting the two liquid phases by the superscripts $^{\alpha}$ and $^{\beta}$,

$$S^{\alpha}_{\mathrm{m}}\mathrm{d}T + (1-x^{\alpha})\mathrm{d}\mu_1 + x^{\alpha}\mathrm{d}\mu_2 = 0 \qquad 4.42.2$$

$$S^{\beta}_{\mathrm{m}}\mathrm{d}T + (1-x^{\beta})\mathrm{d}\mu_1 + x^{\beta}\mathrm{d}\mu_2 = 0 \qquad 4.42.3$$

wherein we have omitted the superscripts on T, μ_1, μ_2 since these have the same values throughout the system. We recall that S^{α}_{m}, S^{β}_{m} denote the proper entropies in the two phases.

To obtain the dependence of γ on the temperature, we have merely to eliminate $\mathrm{d}\mu_1$, $\mathrm{d}\mu_2$ from (1), (2), (3). We thus obtain

$$-\frac{\mathrm{d}\gamma}{\mathrm{d}T}=\frac{\begin{vmatrix} S^{\sigma}_{A} & S^{\alpha}_{\mathrm{m}} & S^{\beta}_{\mathrm{m}} \\ \Gamma_1 & 1-x^{\alpha} & 1-x^{\beta} \\ \Gamma_2 & x^{\alpha} & x^{\beta} \end{vmatrix}}{x^{\beta}-x^{\alpha}}=\frac{\begin{vmatrix} S^{\sigma}_{A} & S^{\alpha}_{\mathrm{m}} & S^{\beta}_{\mathrm{m}} \\ \Gamma_1+\Gamma_2 & 1 & 1 \\ \Gamma_2 & x^{\alpha} & x^{\beta} \end{vmatrix}}{x^{\beta}-x^{\alpha}}. \qquad 4.42.4$$

There seems to be no alternative simpler formula having as high an accuracy.

§4.43 *Accurate formulae*

For the sake of completeness we shall now derive formulae, in principle applicable to any interface in a system of two components, in which we do not neglect the terms in $V\mathrm{d}P$ or $\tau\mathrm{d}P$. We however warn the reader that these formulae are too complicated to be of any practical use.

We accordingly revert to formula (4.36.1), namely

$$-\mathrm{d}\gamma=S^{\sigma}_{A}\mathrm{d}T-\tau\mathrm{d}P+\Gamma_1\mathrm{d}\mu_1+\Gamma_2\mathrm{d}\mu_2 \qquad 4.43.1$$

and formulae (4.36.2) and (4.36.3) applied to each of the two phases α, β

$$\mathrm{d}\mu^{\alpha}_1=-S^{\alpha}_1\mathrm{d}T+V^{\alpha}_1\mathrm{d}P+(\partial\mu^{\alpha}_1/\partial x^{\alpha})\mathrm{d}x^{\alpha} \qquad 4.43.2$$

$$\mathrm{d}\mu^{\alpha}_2=-S^{\alpha}_2\mathrm{d}T+V^{\alpha}_2\mathrm{d}P+(\partial\mu^{\alpha}_2/\partial x^{\alpha})\mathrm{d}x^{\alpha} \qquad 4.43.3$$

$$\mathrm{d}\mu^{\beta}_1=-S^{\beta}_1\mathrm{d}T+V^{\beta}_1\mathrm{d}P+(\partial\mu^{\beta}_1/\partial x^{\beta})\mathrm{d}x^{\beta} \qquad 4.43.4$$

$$\mathrm{d}\mu^{\beta}_2=-S^{\beta}_2\mathrm{d}T+V^{\beta}_2\mathrm{d}P+(\partial\mu^{\beta}_2/\partial x^{\beta})\mathrm{d}x^{\beta}. \qquad 4.43.5$$

We shall also use the Gibbs–Duhem relations for both the phases α, β

$$(1-x^{\alpha})\partial\mu^{\alpha}_1/\partial x^{\alpha}+x^{\alpha}\partial\mu^{\alpha}_2/\partial x^{\alpha}=0 \qquad 4.43.6$$

$$(1-x^{\beta})\partial\mu^{\beta}_1/\partial x^{\beta}+x^{\beta}\partial\mu^{\beta}_2/\partial x^{\beta}=0. \qquad 4.43.7$$

For any variations maintaining equilibrium, we have as usual

$$\mathrm{d}\mu^{\alpha}_1=\mathrm{d}\mu^{\beta}_1=\mathrm{d}\mu_1 \qquad 4.43.8$$

$$\mathrm{d}\mu^{\alpha}_2=\mathrm{d}\mu^{\beta}_2=\mathrm{d}\mu_2. \qquad 4.43.9$$

If we multiply (8) by $1-x^{\beta}$, (9) by x^{β}, substitute from (2), (3), (4), (5), and add, we obtain using (7)

$$\begin{aligned}0=&-\{(1-x^{\beta})(S_1^{\alpha}-S_1^{\beta})+x^{\beta}(S_2^{\alpha}-S_2^{\beta})\}\mathrm{d}T\\&+\{(1-x^{\beta})(V_1^{\alpha}-V_1^{\beta})+x^{\beta}(V_2^{\alpha}-V_2^{\beta})\}\mathrm{d}P\\&+\{(1-x^{\beta})\partial\mu_1/\partial x^{\alpha}+x^{\beta}\partial\mu_2/\partial x^{\alpha}\}\mathrm{d}x^{\alpha}.\end{aligned} \qquad 4.43.10$$

If further we substitute (2), (3) into (1) we obtain

$$\begin{aligned}-\mathrm{d}\gamma=&(S_A^{\sigma}-\Gamma_1 S_1^{\alpha}-\Gamma_2 S_2^{\alpha})\mathrm{d}T-(\tau-\Gamma_1 V_1^{\alpha}-\Gamma_2 V_2^{\alpha})\mathrm{d}P\\&+(\Gamma_1\partial\mu_1/\partial x^{\alpha}+\Gamma_2\partial\mu_2/\partial x^{\alpha})\mathrm{d}x^{\alpha}.\end{aligned} \qquad 4.43.11$$

If we now eliminate dP between (10) and (11) we obtain

$$\begin{aligned}-\mathrm{d}\gamma=&(\Delta_{\alpha\sigma}S-\Delta_{\alpha\sigma}V\Delta_{\alpha\beta}S/\Delta_{\alpha\beta}V)\mathrm{d}T\\&+\{\Gamma_1+\Delta_{\alpha\sigma}V(1-x^{\beta})/\Delta_{\alpha\beta}V\}(\partial\mu_1/\partial x^{\alpha})\mathrm{d}x^{\alpha}\\&+\{\Gamma_2+\Delta_{\alpha\sigma}Vx^{\beta}/\Delta_{\alpha\beta}V\}(\partial\mu_2/\partial x^{\alpha})\mathrm{d}x^{\alpha}\end{aligned} \qquad 4.43.12$$

where we have used the following abbreviations

$$\Delta_{\alpha\beta}S=(1-x^{\beta})(S_1^{\beta}-S_1^{\alpha})+x^{\beta}(S_2^{\beta}-S_2^{\alpha}) \qquad 4.43.13$$

$$\Delta_{\alpha\beta}V=(1-x^{\beta})(V_1^{\beta}-V_1^{\alpha})+x^{\beta}(V_2^{\beta}-V_2^{\alpha}) \qquad 4.43.14$$

$$\Delta_{\alpha\sigma}S=S_A^{\sigma}-\Gamma_1 S_1^{\alpha}-\Gamma_2 S_2^{\alpha} \qquad 4.43.15$$

$$\Delta_{\alpha\sigma}V=\tau-\Gamma_1 V_1^{\alpha}-\Gamma_2 V_2^{\alpha}. \qquad 4.43.16$$

From these definitions we observe that $\Delta_{\alpha\beta}S$ is the entropy increase and $\Delta_{\alpha\beta}V$ the volume increase when unit quantity of the phase β is formed at constant temperature and constant pressure by taking the required amounts of the two components from the phase α. Likewise $\Delta_{\alpha\sigma}S$ is the entropy increase and $\Delta_{\alpha\sigma}V$ the volume increase when unit area of the surface layer σ is formed at constant temperature and constant pressure by taking the required amounts of the two components from the phase α.

Finally we can eliminate $\partial\mu_1/\partial x^{\alpha}$ (or $\partial\mu_2/\partial x^{\alpha}$) between (6) and (12). Thus

$$\begin{aligned}-\mathrm{d}\gamma=&(\Delta_{\alpha\sigma}S-\Delta_{\alpha\sigma}V\Delta_{\alpha\beta}S/\Delta_{\alpha\beta}V)\mathrm{d}T\\&+\{\Gamma_2-x^{\alpha}\Gamma_1/(1-x^{\alpha})+\Delta_{\alpha\sigma}V(x^{\beta}-x^{\alpha})/\Delta_{\alpha\beta}V(1-x^{\alpha})\}(\partial\mu_2/\partial x^{\alpha})\mathrm{d}x^{\alpha}.\end{aligned} \qquad 4.43.17$$

If we vary the temperature and the pressure so as to maintain x^{α} constant, (17) becomes

$$-\mathrm{d}\gamma/\mathrm{d}T=\Delta_{\alpha\sigma}S-\Delta_{\alpha\sigma}V\Delta_{\alpha\beta}S/\Delta_{\alpha\beta}V \qquad (x^{\alpha}\text{ const.}). \qquad 4.43.18$$

This formula applies in principle to any interface. For a liquid–vapour interface we may assume that $\Delta_{\alpha\sigma}V/\Delta_{\alpha\beta}V$ is negligibly small and then (18) reduces to

$$-\mathrm{d}\gamma/\mathrm{d}T=\Delta_{\alpha\sigma}S \qquad (x^{\alpha}\text{ const.}) \qquad 4.43.19$$

which is the same as (4.38.1). For a liquid–liquid interface formula (18), though strictly correct is of little use since the ratio $\Delta_{\alpha\sigma} V/\Delta_{\alpha\beta} V$ of two very small quantities is difficult, if not impossible, to estimate or measure.

§ 4.44 *Solid mixtures*

We turn now to a brief consideration of solid mixtures, especially binary solid mixtures. Much of the treatment of liquid mixtures is directly applicable mutatis mutandis to solid mixtures. Other parts of the treatment are obviously not applicable, in particular osmotic equilibrium and interfacial tensions.

There is a further difference between the treatments of liquid and of solid mixtures, a difference of degree or of emphasis rather than of kind. Most liquids are sufficiently volatile to have conveniently measurable vapour pressures and fugacities. Hence the partial vapour pressures and fugacities of a liquid mixture are familiar experimental quantities. There is consequently a natural and reasonable tendency so far as possible to express most other equilibrium properties in terms of the fugacities. Whereas a few solids also have readily measurable vapour pressures, many are effectively involatile. This being so, there is no particular merit in expressing other equilibrium properties in terms of the fugacities rather than in terms of the absolute activities. If then we compare, for example, the Gibbs–Duhem formula for a binary mixture

$$(1-x)\partial\mu_1/\partial x + x\partial\mu_2/\partial x = 0 \qquad 4.44.1$$

or its corollary

$$(1-x)\partial \ln \lambda_1/\partial x + x\partial \ln \lambda_2/\partial x = 0 \qquad 4.44.2$$

with the Duhem–Margules relation

$$(1-x)\partial \ln p_1/\partial x + x\partial \ln p_2/\partial x = 0 \qquad 4.44.3$$

whereas these three relations are all equivalent, it is natural to place the emphasis on (3) in the case of liquids, but on (1) or (2) in the case of solids.

One of the great similarities between solids and liquids, in contrast to gases, is their insensitivity to pressure. For most purposes we may ignore the pressure. When we do this, a single phase of two components has two degrees of freedom, so that we may use as independent variables T, x. A pair of such phases in equilibrium has then only one degree of freedom, the composition of both phases being determined by the temperature.

We shall deal extremely briefly with the aspects of solid mixtures which are parallel to those of liquid mixtures. We shall quote some formulae without repeating derivations previously given for liquids.

§4.45 *Stationary melting points*

In §4.11 we proved that whenever the relative compositions of a liquid and vapour in mutual equilibrium at a given pressure are identical, the equilibrium temperature is a minimum or maximum at the given pressure. By precisely the same proof the same result can be derived for a solid and vapour in equilibrium.

Of greater practical interest is the equilibrium between solid and liquid phases. Using the superscripts $^{\mathrm{S}}$ and $^{\mathrm{L}}$ to refer to these two phases respectively, we can derive a formula analogous to (4.11.8), namely

$$(S_{\mathrm{m}}^{\mathrm{L}}-S_{\mathrm{m}}^{\mathrm{S}})\mathrm{d}T/\mathrm{d}x=(x^{\mathrm{L}}-x^{\mathrm{S}})(\mathrm{d}\mu_1/\mathrm{d}x-\mathrm{d}\mu_2/\mathrm{d}x) \qquad 4.45.1$$

where x denotes the mole fraction of the component 2 in either phase. Whereas formula (4.11.8) was deduced for constant pressure conditions, as far as (1) is concerned the pressure is practically irrelevant. If the liquid and solid phases have identical compositions then

$$x^{\mathrm{S}}=x^{\mathrm{L}} \qquad 4.45.2$$

and so (1) reduces to

$$(S_{\mathrm{m}}^{\mathrm{L}}-S_{\mathrm{m}}^{\mathrm{S}})\mathrm{d}T/\mathrm{d}x=0. \qquad 4.45.3$$

Since $S_{\mathrm{m}}^{\mathrm{L}}\neq S_{\mathrm{m}}^{\mathrm{S}}$ it follows that

$$\mathrm{d}T/\mathrm{d}x=0. \qquad 4.45.4$$

Thus when the compositions of the solid and liquid in mutual equilibrium are identical, the equilibrium temperature is stationary.

§4.46 *Solid ideal mixtures*

A solid *ideal mixture* is defined in the same manner as in the case of liquids, namely by

$$\Delta_{\mathrm{m}}G=RT\sum_i x_i \ln x_i \qquad 4.46.1$$

and in particular for a binary ideal mixture

$$\Delta_{\mathrm{m}}G/RT=(1-x)\ln(1-x)+x\ln x. \qquad 4.46.2$$

From this definition it follows immediately for a binary mixture that

$$\lambda_1=\lambda_1^0(1-x) \qquad 4.46.3$$

$$\lambda_2=\lambda_2^0 x \qquad 4.46.4$$

where the superscript ^{0} denotes the pure solid phase. Actual examples of ideal mixtures are as few among solids as among liquids, but the ideal mixture remains the convenient standard with which to compare a real mixture.

The thermodynamic functions and properties of ideal mixtures follow directly from (1) or (2) as in the case of liquids. In particular the enthalpies are additive; that is to say the enthalpy of mixing is zero. On the other hand the *proper entropy of mixing* is given by

$$\Delta_\mathrm{m} S/R = -(1-x)\ln(1-x) - x\ln x. \qquad 4.46.5$$

Probably the most important application of this and related formulae is to isotopes, as in §3.55.

§4.47 *Excess functions*

Any real solid mixture, like any real liquid mixture, is conveniently described by the use of excess functions. For a binary mixture these are defined by

$$G_\mathrm{m}^\mathrm{E} = \Delta_\mathrm{m} G - \Delta_\mathrm{m} G^\mathrm{I} = \Delta_\mathrm{m} G - RT\{(1-x)\ln(1-x) + x\ln x\} \qquad 4.47.1$$

$$S_\mathrm{m}^\mathrm{E} = \Delta_\mathrm{m} S - \Delta_\mathrm{m} S^\mathrm{I} = \Delta_\mathrm{m} S + R\{(1-x)\ln(1-x) + x\ln x\} \qquad 4.47.2$$

$$H_\mathrm{m}^\mathrm{E} = \Delta_\mathrm{m} H - \Delta_\mathrm{m} H^\mathrm{I} = \Delta_\mathrm{m} H. \qquad 4.47.3$$

Solid mixtures may be classed, like liquid mixtures, into symmetrical mixtures, including simple mixtures, and unsymmetrical mixtures.