ISOTHERMAL VAPOUR-LIQUIDE PHASE DIAGRAMS DETERMINED STATICALLY BY MEANS OF SPECTROSCOPIC ANALYSIS

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Many methods have been used for the determination of liquid-vapour equilibria, some of them being of a dynamic, while others of a static character [1]. Recent criticisms [2] point out that the latter may be regarded upon as being more reliable, since it seems doubtful whether true equilibria may be reached by the use of dynamic methods. The fulfilment of the well-known Gibbs-Duhem relation is an unambiguous criterion by which to decide whether experimental points of an isothermal phase diagram correspond to true thermodynamic equilibrium. For this test to be accurate, activity coefficients both in the liquid and vapour phases must be taken into consideration. Now, in the pressure ranges met with in liquid-vapour equilibria, the variation of these coefficients with pressure is but slight, whereas their dependence on temperature is much more pronounced so that isobaric (boiling point) diagrams are not very suitable for exact thermodynamical analysis. Though it is not altogether impossible to construct isothermal diagrams from data obtained by dynamic methods, the static ones are more suitable for this purpose since they yield such diagrams immediately and are thus superior in this respect, too.

The difficulty met with in the static methods lies in the sampling of the vapour, in view of the exceedingly small amount of matter being present as vapour in vessels of customary size.* The optical method we have evolved avoids sampling altogether. The liquid mixture of desired composition is filled into a tube with planparallel quartz windows (Fig. 1) and freezed out there with liquid air in order that air could be removed by pumping. Then the tube is brought to the desired temperature so that the empty space left above the liquid is filled with its vapour, the amount of liquid having been chosen so that determination of the ultraviolet absorption spectrum of the vapour may be effectuated through the quartz windows. Only compounds containing conjugated double bonds (or aromatic rings) can, of course, be investigated by ultraviolet spectroscopy.

The quantitative analysis based on the absorption spectra has been carried out by a method described previously [4]. For every component a suitable

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*Such problems are usually solved by radioactive tracer methods, and only in some special cases by classical ones [3].

characteristic band is chosen and the blackness of the photographic plate mea-
sured at its maximum together with that of the neighbouring minimum. It is
evident that, with a cell of given thickness, the differences $\Delta F = \log \dfrac{I_{min}}{I_{max}}$
are proportional to the vapour concentration, quite in the same way as if one
would reckon with the difference between the blackness of the maximum and
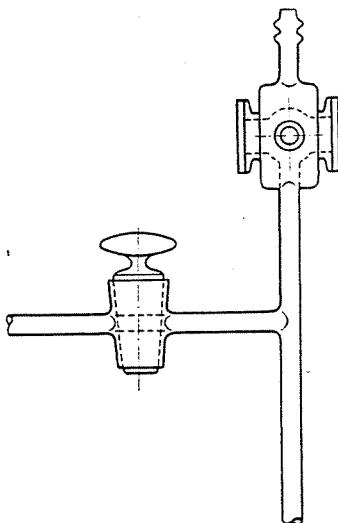that of an exposure made in vacuo or through a spectroscopically inactive medium

Fig. 1

at the wavelength of the maximum. By photographing the spectrum of the vapour
of the pure components, too, at the same temperature and using the same cell,
the relative concentration a can be easily computed as the ratio of the differences
in blackness :

$$\frac{\Delta F_i}{\Delta F_i^0} \equiv a_i = \frac{c_i}{c_i^0} . \tag{1}$$

Here subscript i denotes the component under question and superscript o refers
to its pure state, at the same temperature.

It would be easy to calculate partial pressures p_i, mole fractions y_i and
the total pressure $P = \Sigma p_i$, by beginning with the relation

$$p_i = RT\, c_i , \tag{2}$$

provided the vapour could be treated as a perfect gas. For purposes of the
exact thermodynamical test mentioned above, this approximation is, however,

not permissible. Concentrations and mole fractions are related for any kind of mixture by the equation :

$$c_i = \frac{n_i}{nV} = \frac{y_i}{V}\,,\tag{3}$$

the n_i being numbers of moles present $(n = \Sigma n_i)$, and V the molar volume of the mixture. Now, for a mixture of real gases under not too high a pressure, so-called ideal behaviour may be safely assumed. This means that V can be expressed according to Amagat's rule :

$$V = \frac{RT}{P} \sum y_i z_{i,P}\tag{4}$$

where $z_{i,P}$ is the so-called compressibility factor of the ith component when in pure state, under the total pressure P. Substituting (4) and (3) :

$$c_i = \frac{y_i P}{RT \Sigma y_i z_{i,P}}\,.\tag{5}$$

Similarly, we can write for the saturated vapour concentration of the pure substance i, at the same temperature :

$$c_i^0 = \frac{p_i^0}{RT\, z_{i,p_i^0}} \equiv \frac{p_i^*}{RT}\,.\tag{6}$$

p_i^0 denoting the vapour pressure of pure i, and p_i^* being an abridged notation for $p_i^0/z_{i,p_i^*}$.

So we have instead of (1) :

$$a_i \equiv \frac{c_i}{c_i^0} = \frac{y_i P}{p_i^* \Sigma y_i z_{i,P}}\tag{7}$$

or :

$$a_i p_i^* = \frac{y_i P}{\Sigma y_i z_{i,P}}\,.\tag{8}$$

By the definition of mole fractions $\Sigma y_i = 1$, so it follows from (8) :

$$\Sigma a_i p_i^* = \frac{P}{\Sigma y_i z_{i,P}}\,,\tag{9}$$

and this, combined with (8), gives :

$$y_i = \frac{a_i p_i^*}{\Sigma a_i p_i^*}\,.\tag{10}$$

We remember that the values a_i are the relative concentrations determined spectroscopically, so it may be seen that the vapour pressures of the components in their pure states must be known in order to make calculation of the molar composition of the vapour possible. The compressibility factors z_i, P_i^0, which are needed also for this calculation may be taken with reasonable accuracy from the respective generalized chart.

Based on eq. (9), the total vapour pressure P may be calculated by successive approximation. As a first approximation, the factors $z_{i,P}$ may be taken as unity by which the whole divisor on the right hand side becomes unity and thus the left hand side gives immediately a first value for P. With factors $z_{i,P}$, belonging to this value of P (as read from the generalized compressibility chart), the sum $\Sigma y_i z_{i,P}$ is formed and substituted into (9), giving thus a second approximation for P. In the actual example to be cited below, this second approximation proved to be satisfactory already, due to the fact that the highest value of P did scarcely exceed one tenth of an atmosphere (see Table 2). There is obviously no difficulty for carrying approximation further beyond, if necessary.

Condition of equilibrium between vapour and liquid being equality of fugacities, these latter have to be calculated for the components of the vapour. In the range of validity of Amagat's rule, this can be done by use of the rule of Lewis and Randall. In our special case, where pressures were well below one atmosphere, fugacity coefficients could be taken, moreover, equal to the compressibility coefficients, so that the expression of the fugacity of the ith component in the vapour becomes:

$$f_i = z_{i, P} y_i P . \qquad (11)$$

Usually in isothermal vapour pressure diagrams curves of the partial pressures are shown also, together with that of the total pressure. Whereas in the case of a mixture of perfect gases partial pressures are defined unambiguously by Dalton's law, this law does not hold for real mixtures and another suitable definition must be sought. We must point out that partial pressures are, in general, not more than defined quantities which cannot be measured directly, owing to the lack of suitable semipermeable membranes. The most current definition is that given by Bartlett's rule, which is, however, not in concordance with Amagat's rule. We are proposing a new definition which has the advantage of meeting this latter requirement. It seems clear that for a real mixture the simple equation (2) has to be corrected by a suitable compressibility factor, the only question being to which pressure this factor has to belong. If concentration is expressed according to Amagat's rule by equation (5), then the further requirement that the sum of the partial pressures must be equal to the total pressure decides this question without any doubt : the compressibility factor

has to be taken at the total pressure of the mixture, that is :

$$p_i = z_{i, P} RT c_i = \frac{y_i z_{i, P}}{\Sigma y_i z_{i, P}} P = z_{i, P} a_i p_i^* \tag{12}$$

the latter expression following from (8).*

Our next problem is the determination of the fugacities or else of the rational activity coefficients in the liquid mixture of known composition, in equilibrium with the vapour. In the case of an ideal mixture, the fugacity of each component is smaller than in its pure state, in the proportion of its mole fraction x_i :

$$f_{i, P} = x_i f_{i, P}^0 \tag{13}$$

If the mixture is not an ideal one, then x_i has to be replaced by the activity : $a_i = \gamma_i x_i$, γ_i being the activity coefficient. It must be considered, however, that the fugacity $f_{i,P}$ of the pure liquid is not identical with the fugacity of its saturated vapour, the pressure of the latter (p_i^0) not being equal to P, the pressure of the mixture. On the assumption that the liquid is incompressible, we have for the difference (V_i^0 is the molar volume of the liquid) :

$$\ln \frac{f_{i, P}^0}{f_{i, p_i^0}^0} = \int_{p_i^0}^{P} \frac{V_i^0}{RT} dP = \frac{V_i^0 (P - p_i^0)}{RT} \tag{14}$$

The fugacity f_{i, p_i^0} may be, on the other hand, expressed as :

$$f_{i, p_i^0}^0 = z_{i, p_i^0} p_i^0 \tag{15}$$

on the condition that the pressure is low enough so that the fugacity coefficient may be taken equal to the compressibility coefficient (cf. eq. 11).

We have thus, instead of (13) :

$$f_{i, P} = \gamma_i x_i z_{i, p_i^0} p_i^0 \exp \left[\frac{V_i^0 (P - p_i^0)}{RT} \right]. \tag{16}$$

We must point out, incidentally, that the definition of activity given here is not the usual one, the standard state being not fixed at 1 atmosphere, but taken every time at the pressure P just prevailing. We made this choice in order that

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* Numerical computation by successive approximation may be based alternatively on eq. (12). As the first approximation the $z_{i,P}$ are taken equal to unity, i. e. $p_i = a_i p_i^*$ and $P = \Sigma p_i = \Sigma a_i p_i^*$. With values of the $z_{i,P}$ corresponding to this first P, the p_i are recalculated, etc.

only departures from ideal behaviour may be expressed by the activity coefficients γ_i. In order to refer activities to the usual standard state, the right hand
side of equation (16) had to be multiplied by the factor

$$\exp\left[-\frac{V_i^0(P-1)}{RT}\right].$$

Condition of thermodynamic equilibrium is equality of the fugacities as
expressed by (11) and (16), respectively. By equating the right hand sides and
solving for γ_i, we get :

$$\gamma_i = \frac{y_i z_{i,P} P}{x_i z_{i,p_i^0} p_i^0}\exp\left[\frac{V_i^0(p_i^0-P)}{RT}\right]. \tag{17}$$

If experimental data correspond to true equilibrium, then the values of
γ_i calculated by (17) must fulfill the well-known Gibbs—Duhem relation :

$$\Sigma x_i d\mu_i = RT \Sigma x_i \frac{\partial \ln(\gamma_i x_i)}{\partial x_i} dx_i = RT \Sigma x_i \frac{\partial \ln\gamma_i}{\partial x_i} dx_i = 0. \tag{18}$$

For a two-component system, especially, for which $dx_1 = -dx_2$, eq. (18)
results in the following simpler relation :

$$\left(\frac{\partial \ln\gamma_1}{\partial \ln x_1}\right)_{P,T} = \left(\frac{\partial \ln\gamma_2}{\partial \ln x_2}\right)_{P,T} \tag{19}$$

the two differential quotients being taken at the same point of composition, i. e. at the same temperature and pressure. When the calculated
data are represented in a diagram with coordinates $\log x$ and $\log \gamma$,
respectively, and the points connected by smooth curves for each component, then the slope of these curves pertaining to points of the same
composition must be parallel in the case that the data correspond to
true equilibrium.

In order to try the reliability of our optical method, we determined the
vapour pressures of mixtures of benzene and chlorobenzene by it, at 26° C.
This temperature was 1° below that of our room, some difference being necessary
in order to avoid condensation of the vapour on the quartz windows which
were not tempered (see Fig. 1).

Choice of a greater difference, on the other hand, was prohibited by the
fact that the outstanding stem of our cell was not tempered either. Samples
of 0,4 ml liquid were introduced through the cell into the vessel and freed of
air by freezing out repeatedly with liquid air, under vacuum, the quartz windows

being sealed off by rubber washers. The stopcock was closed when thawing the sample. At last, the liquid sample was introduced into the cell by tilting over the vessel, carefully avoiding any contamination by stopcock-grease. The cell had a circular groove in order to prevent the liquid to come into contact with the rubber washers and quartz windows. For the measurements, the cell was fixed in its upturned position and tempered with flowing water.

Two exposures were made with each sample and photometer readings taken on their magnified projections so that the photometer slit could be brought into three different positions on each band. We had thus six parallel readings for each point, by which procedure the error of the mean values of the differences ΔF could be reduced to about 0,005. As analytical bands, the following ones were chosen : $0\text{-}0$ for chlorobenzene, B_0^0, A_0^1 for benzene, these latter three given here in the order of increasing intensity.* The ΔF values found are shown in Table I. It may be seen, that determination of the relative concentration of chlorobenzene could be done in a quite straightforward manner, the absorption of benzene having practically equal strength at the maximum of the $0\text{-}0$ band of C_6H_5Cl and at the neighbouring minimum, respectively.

Table I

$\Delta F = \log \dfrac{I\text{min}}{I\text{max}}$ values for the analytical bands of the pure components

Band	0—0	B°	A¹	A°
Chlorobenzene	0,507	—0,038	—0,025	0,030
Benzene	0,001	0,314	1,60 (calc.)	4,83 (calc.)

The situation is not quite as favourable in the case of benzene, the absorption of chlorobenzene being not uniform in the neighbourhood of the chosen analytical bands.

The necessary correction could be applied, however, without difficulty, since the relative concentration of chlorobenzene could be calculated as said above. The bands A_0^1 and A_0^0 were, with the cell used, so strong in the case of pure benzene, that they fell beyond the straight part of the optical density curve. The values given in the table are calculated from exposures made with mixtures, whose vapour contained benzene to a suitably smaller concentration,

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* Band B_0^0 corresponds to a transition for which the normal vibration No 18 (numbered according to Herzberg) is excited with $v = 1$ and the others are unexcited in the ground state, while in the electronically excited upper state all vibrations are on the zero level. For band A_0^0 the situation is just reversed, vibration No 18 being at the level $v = 1$ in the electronically excited state. The transition corresponding to band A_0^1 differs from that connected with A_0^0 in so far as vibration No 20 is on the level $v = 1$, both in the ground and electronically excited states. Statistical frequency of excited vibrations being small at room temperature, this fact alone is sufficient to account for the greater intensity of band A_0^0.

this latter having been determined from the intensity of band B_0^0. All exposures, those with the pure components as well as those with the series of mixtures
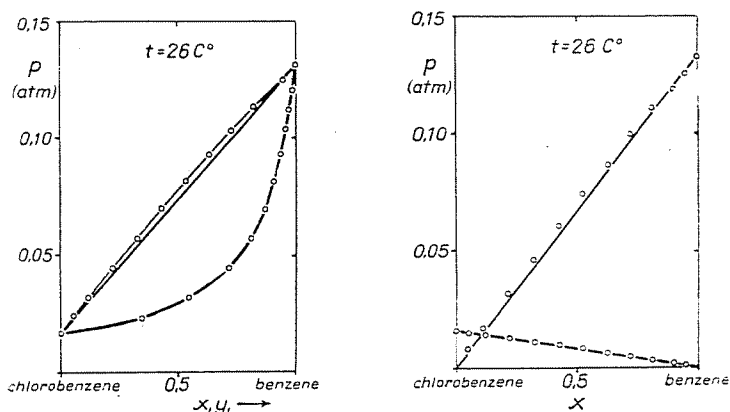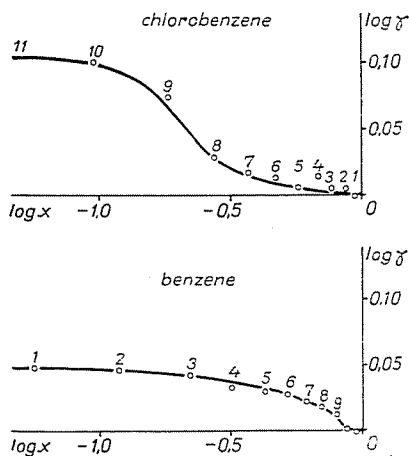

Fig. 2

Fig. 3

of different composition, were made on a single plate, thus avoiding further errors due to differences in the characteristics of individual plates.

In order to compute activity coefficients, composition of the liquid phase must be known also. This composition was taken as being identical with that of the mixture introduced into the vessel, i. e. the change in composition caused by partial evaporation has been neglected. It did not seem worth while to correct these values, since the amount evaporated could be estimated to lie but between 1 and 0,1 per cent (liquid introduced being about 4 millimoles,

against 0,04 millimoles of saturated vapour filling the volume of 8 ml of the vessel in the case of pure benzene, and 0,005 millimoles in the case of pure chlorobenzene). At those compositions where the amount of vapour is greater, the difference between liquid and vapour is relatively smaller, so that the change in composition caused by evaporation could not grow beyond some units in the fourth decimal of the mole fraction.

The calculated values of vapour pressures and activity coefficients are summarized in Table II, and shown graphically in Figs. 2 and 3. On the left part of Fig. 2, partial pressures may be seen as calculated according to (12) whereas on the right part the total pressure P is represented as a function of both x and y. The straight lines drawn in the figure would correspond to ideal behaviour, and it may be seen that our system shows slight positive deviations.

<center>Table II</center>

Chlorobenzene Benzene		p° atm 0,0163 0,1315		P_k atm 44,6 47,7	ϑ 0,47 0,53	$z_p o^*$ 0,9993 0,9956	ϱ g/ml 1,107 0,879		V° lit 0,1016 0,0888	
x_1	a_i	$a_i p_i^*$	P_l atm	y_i	$z_i P_l$,	P atm	p_i atm	γ_i	$\log \gamma_i$	$-\log x_i$
0,0492	0,0690	0,0011	) ,1	0,0088	0,9949	0,1251	0,0011	1,391	0,1433	1,3083
0,9508	0,9427	0,1245		0,9912	0,9958		0,1240	0,992	—0,0035	0,0220
0,0958	0,1203	0,0020	0,1206	0,0166	0,9951	0,1201	0,0020	1,246	0,0955	1,0187
0,9042	0,8981	0,1186		0,9834	0,9960		0,1181	0,994	—0,0026	0,0440
0,1846	0,2191	0,0036	0,1138	0,0316	0,9954	0,1134	0,0036	1,178	0,0712	0,7339
0,8154	0,8344	0,1102		0,9684	0,9962		0,1098	1,025	0,0107	0,0886
0,2773	0,2940	0,0048	0,1032	0,0465	0,9958	0,1029	0,0048	1,053	0,0224	0,5574
0,7227	0,7450	0,0984		0,9535	0,9965		0,0981	1,033	0,0141	0,1414
0,3719	0,3868	0,0063	0,0926	0,0680	0,9963	0,0923	0,0063	1,024	0,0145	0,4300
0,6281	0,6535	0,0863		0,9320	0,9969		0,0860	1,043	0,0163	0,2023
0,4692	0,4834	0,0079	0,0819	0,0965	0,9967	0,0817	0,0079	1,025	0,0107	0,3289
0,5308	0,5600	0,0740		0,9035	0,9973		0,0738	1,059	0,0249	0,2751
0,5696	0,5760	0,0094	0,0697	0,1349	0,9972	0,0696	0,0094	1,007	0,0030	0,2448
0,4304	0,4565	0,0603		0,8651	0,9977		0,0602	1,065	0,0274	0,3664
0,6751	0,6943	0,0113	0,0571	0,1979	0,9977	0,0570	0,0113	1,025	0,0107	0,1709
0,3249	0,3465	0,0458		0,8021	0,9981		0,0457	1,072	0,0302	0,4886
0,7804	0,7870	0,0128	0,0443	0,2889	0,9982	0,0443	0,0128	1,006	0,0026	0,1078
0,2196	0,2385	0,0315		0,7111	0,9985		0,0315	1,093	0,0386	0,6586
0,8832	0,8895	0,0145	0,0314	0,4618	0,9987	0,0314	0,0145	1,006	0,0026	0,0542
0,1168	0,1280	0,0169		0,5382	0,9989		0,0169	1,104	0,0430	0,9326
0,9446	0,9389	0,0153	0,0234	0,6538	0,9991	0,0234	0,0153	0,994	—0,0026	0,0250
0,0554	0,0610	0,0081		0,3462	0,9992		0,0081	1,109	0,0449	1,2567

* Calculated by linear interpolation

These deviations show up much more markedly in the $\log \gamma - \log x$ diagram of Fig. 3, and so do the errors of the experimental values. The deviations of the experimental points from smooth curves are, however, well within the limit of error 0,005 for $\varDelta F$, mentioned above.* The smooth curves of Fig. 3 have been drawn through the experimental points so that at the limit Raoult's law should be satisfied, according to which $\log \gamma$ must tend asymptotically to zero at the limit $x = 1$ ($\log x = 0$), and at the same time, the slope must become zero at the limit $x = 0$ also, according to Henry's law. Points belonging to identical compositions are numbered alike on both curves. An inspection of the figure shows that tangents drawn at such pairs of points are parallel indeed within the limits of accuracy of our measurements. This means that the requirements of the Gibbs-Duhem relation are fulfilled, i. e. our data represent true thermodynamic equilibrium.

Summary

Exact thermodynamical relations are derived by which isothermal vapour pressure diagrams of liquid mixtures can be constructed and activity coefficients calculated, based solely on the knowledge of the volume concentrations of the components in the saturated vapour. An optical method for determining these concentrations is described. Application to the actual system benzene-chlorobenzene proves that data determined statically by this method correspond to true thermodynamical equilibrium, as they comply with the Gibbs—Duhem relation.

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* This is also true for the scattering of the experimental points of chlorobenzene : for a mixture containing but 5% chlorobenzene, the uncertainty of $\varDelta F$ may cause a relative error of 20%. This scattering is not perceptible on the equilibrium diagram (Fig. 2), because the points with considerable scattering belong to very small partial pressures. The data could be computed with greater accuracy for benzene, especially in those regions where the intensive bands A_0^0 and A_0^1 could be used, i. e. in the range of smaller benzene contents. So, on the whole, results are more precise in the case of samples containing more chlorobenzene.