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TERNARY MASS TRANSFER IN LIQUID–LIQUID EXTRACTION

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Abstract—Isothermal interphase mass transfer measurements were carried with the partially miscible Type I system glycerol (1)–water (2)–acetone (3) in a modified batch Lewis extraction cell. Three types of experiments were performed:

(A) in which the acetone-rich phase was saturated and the initial glycerol-rich phase composition lay on the extension of the corresponding tie-line,

(B) in which the glycerol-rich phase was saturated and the initial acetone-rich phase composition lay on the extension of the corresponding tie-line and

(C) in which initially both the acetone-rich and glycerol-rich phases were unsaturated.

The equilibration trajectory was monitored in both phases by sampling at suitable intervals. In experiments A and B rectilinear equilibration trajectories were obtained while in the experiment C the approach towards equilibrium was highly curvilinear in the composition space.

A theoretical model, based on irreversible thermodynamics and allowing for diffusional coupling between species transfers, is developed to simulate the three types of experiments above. The matrix of equilibration rate constants, in either fluid phase, is re-constructed by determining the eigenvectors and eigenvalues from experimental observations. It is found that both matrices of rate constants in the acetone-rich and glycerol-rich phases have extremely large off-diagonal elements. It is stressed in the discussions that the experimental results cannot be explained, even qualitatively, without inclusion of these off-diagonal contributions.

Some interesting mass transfer phenomena in the region of the plait point are pointed out and the need for a fundamental irreversible thermodynamics approach to interphase mass transfer is emphasised. It is concluded that rigorous mass transfer formulations, allowing for diffusional coupling, will be required to be incorporated into design of extractors involving highly non-ideal liquid mixtures.

INTRODUCTION

In three publications [1–3] in recent years we have presented experimental evidence for mass transfer in ternary distillation (in sieve tray and wetted-wall columns) and in ternary absorption/condensation (in wetted-wall column) to demonstrate the peculiar transfer characteristics of multicomponent mixtures, of which a three-component system forms the simplest case. Experimental confirmation was presented for three interaction phenomena, characteristic of multicomponent mixtures: *reverse diffusion* (transfer of a component against its composition driving force), *osmotic diffusion* (diffusion of a component in the absence of a composition driving force) and *diffusion barrier* (a component does not diffuse even though a driving force exists for its transfer). The practical consequences of these interaction phenomena include the possibility that the point Murphree efficiency of a component could assume values exceeding unity or even vanish or assume negative values. In an early computational study Toor and Burchard [4] showed with the aid of a design example with the system methanol–*iso*-propanol–water that neglect of multicomponent interaction effects could lead to severe underdesign.

The modelling of the interphase mass transfer processes in non-ideal multicomponent systems requires a fundamental basis in irreversible thermodynamics [5–7] and the matrix of transfer coefficients in a given fluid phase has to allow for non-zero off-diagonal elements. Pseudo-binary approaches to multicomponent mass transfer, e.g. by use of effective diffusion coefficients, have been shown to fail even at the qualitative level [1–3]. Quantitative confirmation of the mass transfer models developed at UMIST [8, 9] have also been published by other research workers [10–17]. Design procedures for distillation and condensation equipment with the inclusion of these mass transfer models have also been presented [18–23].

One further important practical application of multicomponent mass transfer is in liquid–liquid extraction. Such systems are necessarily thermodynamically non-ideal and it must be expected that diffusional coupling would be important in such systems. An early publication originating from our laboratories reported experimental data for the system glycerol–water–acetone in a batch extraction cell and demonstrated that the results could only be explained by considering diffusional coupling effects [24]. The theoretical analysis of this paper was however fundamentally wrong due to an incorrect application of the Onsager reciprocal relations to interphase mass transfer processes. This error was noted subsequently [8].

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The values of the matrix of mass transfer coefficients reported earlier [24] are therefore incorrect, though the broad qualitative conclusions of the paper remain valid.

In the present communication we develop an alternative approach to the determination of the matrix of mass transfer coefficients in either fluid phase. This new approach was inspired by the elegant analysis of Wei and Prater [25] for the determination reaction rate constants in complex reacting systems. To demonstrate the utility of our approach further experimental data for the system glycerol – water – acetone were obtained. We also took the opportunity of improving the accuracy of our liquid–liquid equilibrium data fitting by performing additional equilibrium experiments.

We give a brief outline of our experimental procedure before developing our theoretical analysis.

EXPERIMENTAL

The extraction measurements were carried out in a modified batch Lewis extraction cell with a capacity of about 6000 ml and equipped with two turbine stirrers which can be either co- or counter-rotated; see Fig. 1. Vertical baffles aid the efficient mixing of the bulk phases and a horizontal ring and disc baffle at the interface provide the calming action necessary to avoid rippling of the annular liquid–liquid interface. The ratio of the stirrer speeds can be varied and the stirrers were run at the maximum frequencies possible without agitating the interface. Because large volume changes may occur during the extraction the horizontal baffle system was made vertically movable over wide limits so that the interface could always be kept at the middle of the ring and disc baffles throughout the extraction process. Representative samples of the bulk phases were withdrawn through sampling tubes at suitable intervals during the equilibration process. The whole extraction cell was thermostatted at 25°C and the stirrer drive provided by a regulated motor with a frequency checked by a timer counter with a photocell pick-up from a striped disc on a drive sheave.

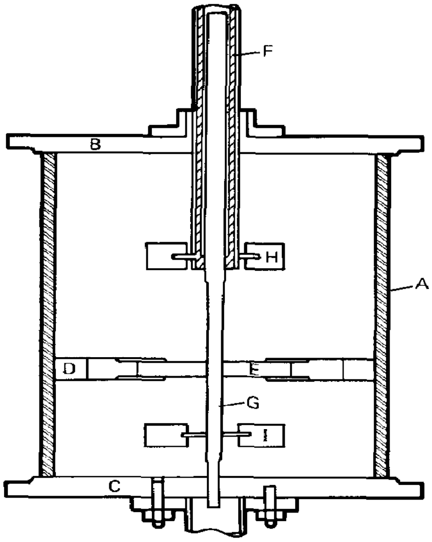

Fig. 1. Modified Lewis extraction cell. (A) Glass cylinder; (B) top plate; (C) bottom plate; (D) movable interfacial ring; (E) central baffle; (F) upper phase stirring shaft; (G) lower phase stirring shaft; (H) upper phase turbine stirrer; (I) lower phase turbine stirrer.

The samples were analysed by determining their density in Lipkin and capped bottle pycnometers and their refractive indices in a Zeiss dipping refractometer with a set of thermostatted prisms. By using a number of precautions especially with the refractometer measurements, standard deviations of 0.00015 g ml^{-1} and 0.000019 for the density and refractive index determinations, respectively, were obtained consistently. The compositions (expressed in mole fractions) were represented by fifth order orthogonal polynomials of the density and refractive index in x_1, x_2. The resultant standard deviation of the composition determinations as found from the analysis of mixtures of known compositions were

$$\sigma_{x_1} = 0.0015; \quad \sigma_{x_2} = 0.0041; \quad \sigma_{x_3} = 0.0044$$

for the three components glycerol (1), water (2) and acetone (3), respectively.

The heavier glycerol-rich phase (of known amount and composition) was introduced at the bottom of the cell and the lighter acetone-rich phase (known amount and composition) was introduced at the top of the cell. The drive was started and the extraction allowed to proceed. Samples were withdrawn at suitable intervals from both phases and the compositions analysed to determine the equilibration trajectory.

In addition to the equilibration measurements described above, the liquid–liquid equilibrium data were measured; Fig. 2 shows the tie-line data for the system. Further details on the equilibrium measurements and on the experimental procedures adopted in the extraction measurements are available elsewhere [26].

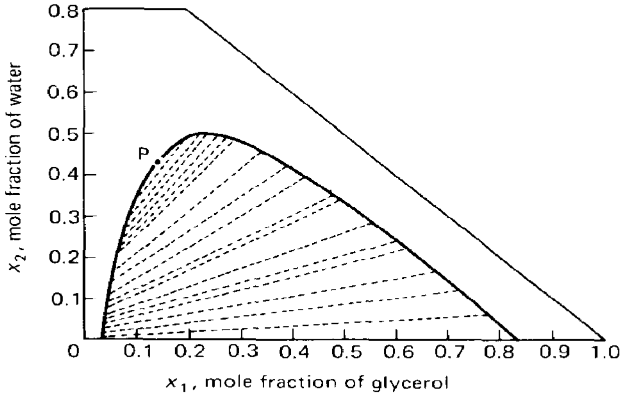

Fig. 2. Equilibrium tie-line data for the system glycerol (1)–water(2)–acetone(3). P is the plait point with the composition $x_1 = 0.1437$, $x_2 = 0.4291$, $x_3 = 0.4272$.

THEORETICAL MODEL DEVELOPMENT AND ANALYSIS OF EXPERIMENTAL RESULTS

Before discussing the results of the experimental runs on the equilibration process during extraction we shall develop the theoretical framework for the analysis of the results; the experimental runs were chosen to provide crucial tests of the theoretical predictions.

The initial amounts and compositions of each phase are fixed and known from experiment. If the comparitively small amounts of the samples withdrawn from either phase are neglected, the extraction cell can be considered to be a closed system in which the total and constituent masses are constant and equal to the initial amounts M_{t0} and M_{i0}, respectively. At any given time therefore

$$M_t' + M_t'' = M_{t0} \tag{1}$$

and

$$M_i' + M_i'' = M_{i0}; \quad i = 1, 2, 3 \tag{2}$$

where the superscripts $'$ and $''$ are used to denote the acetone-rich and glycerol-rich phases respectively. If x_i represents the bulk liquid phase composition, then this will very nearly equal the average composition of the particular phase and we may write

$$M_i' = x_i' M_t'; \; M_i'' = x_i'' M_t''; \quad i = 1, 2, 3 \tag{3}$$

and eq. (2) may be replaced by the conservation relationship

$$x_i' M_t' + x_i'' M_t'' = M_{i0} = x_{i0} M_{t0}; \quad i = 1, 2, 3 \tag{4}$$

where x_{i0} represents the initial composition of the mixture of the two phases. There are only two independent material balance relationships from the set of eqs (1) and (4). It is to be noted that all the quantities on the left-hand side of the above equations are functions of time.

Now, if A represents the interfacial area between the two liquid phases we can calculate the interfacial molar fluxes of the individual components, N_i, in either fluid phase

$$N_i = \frac{1}{A}\frac{dM_i}{dt}; \quad i = 1, 2, 3. \tag{5}$$

Similarly the mixture molar flux in either fluid phase is

$$N_t = \frac{1}{A}\frac{dM_t}{dt} = \sum_{i=1}^{n} N_i. \tag{6}$$

From the material balance relations (1) and (2) we see that

$$N_t' + N_t'' = 0 \tag{7}$$

and

$$N_i' + N_i'' = 0; \quad i = 1, 2, 3 \tag{8}$$

i.e. the rates of transfer in one phase must be negative of the corresponding rate for the other. In addition to the molar fluxes N_i, relative to the laboratory fixed coordinate reference frame, we can calculate molar diffusion fluxes J_i with respect to the molar average mixture velocity, thus:

$$J_i \equiv N_i - x_i N_t; \quad i = 1, 2, 3 \tag{9}$$

where we note because $J_1 + J_2 + J_3 = 0$, only two of the J_i, in either fluid phase, are independent. From eqs (5), (6) and (9) we get

$$J_i = \frac{1}{A} M_t \frac{dx_i}{dt}; \quad i = 1, 2. \tag{10}$$

If the driving force for mass transfer is taken as the difference in compositions between the interface and the bulk fluid phase, $x_{iI} - x_i$, the interphase transfer rate relations may be written in the form

$$(J) = c_t [k] (x_I - x) \tag{11}$$

where we have adopted two-dimensional matrix notation. The extraction process will be described by two matrices of mass transfer coefficients: $[k']$ in the acetone-rich phase and $[k'']$ in the glycerol-rich phase.

Let us now examine the structure of the matrix $[k]$ in either fluid phase. If the interphase mass transfer process is considered to be quasi-steady state, then $[k]$ will be given by

$$[k] = \frac{[D]}{\delta} \tag{12}$$

where δ is the effective "film" thickness and $[D]$ is the matrix of Fickian diffusivities. It is shown in Appendix A, using the theory of irreversible thermodynamics, that for the system glycerol–water–acetone the matrix of Fickian diffusivities $[D]$ must be expected to have significant off-diagonal elements D_{12} and D_{21}. Since $[k]$ is directly proportional to $[D]$ in the film theory, we must expect the structure of $[k]$ to include significant off-diagonal elements too.

If on the other hand a surface renewal type mechanism governs the transfer process, as is likely to be the case for the stirred cell, then the matrix $[k]$ will show a square-root dependence on $[D]$:

$$[k] = [D]^{\frac{1}{2}} s^{\frac{1}{2}}$$

where s is the renewal frequency. In this case, because of the weaker dependence on the molecular diffusivities, the cross-coefficients will be smaller (in proportion to the diagonal coefficients) than in the film model for transfer. Nevertheless the cross-coefficients k_{12} and k_{21} will still remain finite.

Other factors such as surface instabilities will also determine the structure of $[k]$. Sethy and Cullinan [27] found that though the measured $[D]$ for the system acetonitrile–benzene–n-heptane has sizable off-diagonal elements, extraction trajectories in a Lewis stirred cell could be interpreted by assuming vanishing off-diagonal elements in $[k]$. They ascribed this nonconformity in the structure between $[k]$ and $[D]$ to Marangoni instabilities which reduced molecular diffusional coupling. We obtained Schlieren data to verify that our experiments with glycerol–water–acetone were not influenced by Marangoni type instabilities. We should on the basis of the above discussions expect the structure of $[k]$ to include sizable off-diagonal elements. One of the major objectives of the experimental study is to verify this expectation and to determine the significance of the cross-coefficients in determining the extraction trajectories.

Introducing eq. (11) into eq. (10) and expressing the result in two-dimensional matrix notation we get the differential equation describing the transient diffusion process in either phase:

$$\frac{\mathrm{d}(x)}{\mathrm{d}t} = \frac{c_t[k]A}{M_t}(x_\mathrm{I} - x). \tag{13}$$

During the extraction process, c_t, $[k]$ and M_t, in either fluid phase can all be expected to vary. Also, there is no requirement that the interfacial composition $x_{i\mathrm{I}}$ instantaneously attains the final equilibrium state, corresponding to either end of the appropriate tie-line. Put another way, we should expect the interfacial state to vary during the extraction process, with a gradual approach to the final equilibrium state at the interface. The interpretation of the extraction experiments taking into proper account the transient variations of c_t, $[k]$, M_t and $x_{i\mathrm{I}}$ is a formidable task. Keeping in mind that our objective in the experimental study was to determine the influence of coupling effects, signified by the cross-coefficients k_{12} and k_{21}, we chose an alternative approach to the solution of the differential eq. (13) by making the following simplifications:

(i) That the "volumetric" mass transfer coefficient matrix $[K]$:

$$[K] = \frac{c_t[k]A}{M_t} \tag{14}$$

remains constant during the extraction process. This essentially means that our results yield some integral averaged value for each phase: $[K']$ for the acetone-rich phase and $[K'']$ for the glycerol-rich phase. One test of the validity of this assumption will be the success, or failure, of the model assuming constant $[K]$ to reproduce the experimentally observed trajectories.

(ii) We assume in the ensuing analysis that the interface instantly attains its final equilibrium state and remains invariant throughout the extraction process. This assumption is most likely to be in error during the initial stages of the extraction process. Taking into consideration the fact that each equilibration run to be discussed later lasts for about 6 h, we feel that the assumption of constant $x_{i\mathrm{I}}$ will not have a significant effect on the final calculated values of $[K]$.

With the above two key assumptions we obtain the *linear*, two-dimensional, matrix differential equation

$$\frac{\mathrm{d}(x)}{\mathrm{d}t} = [K](x_\mathrm{I} - x) \tag{15}$$

subject to the initial condition

$$t = 0,\ (x) = (x_0);\ (x_\mathrm{I} - x) = (x_\mathrm{I} - x_0). \tag{16}$$

To solve eq. (16) we proceed by first determining the eigenvalues λ_1 and λ_2 and eigenvectors (e_1) and (e_2) of $[K]$. The eigenvalues are given by

$$\lambda_1, \lambda_2 = \frac{K_{11} + K_{22}}{2} \pm \frac{K_{11} - K_{22}}{2} \times \sqrt{1 + \frac{4K_{12}K_{21}}{(K_{11} - K_{22})^2}}. \tag{17}$$

The eigenvectors (e_i), corresponding to λ_i, is only determined to an arbitrary scalar multiplier and its direction is given by

$$(e_i) = \begin{pmatrix} -\dfrac{K_{12}}{K_{11} - \lambda_i} \\ 1 \end{pmatrix} \equiv \begin{pmatrix} -\dfrac{K_{22} - \lambda_i}{K_{21}} \\ 1 \end{pmatrix};\quad i = 1, 2. \tag{18}$$

We construct the modal matrix $[E]$ of $[K]$ by placing (e_1) and (e_2) in order, i.e.

$$[E] = [(e_1)\ (e_2)] \tag{19}$$

which has the property that

$$[E]^{-1}[K][E] = [\lambda] \tag{20}$$

where $[\lambda]$ is a diagonal matrix with the eigenvalues λ_1 and λ_2 on its principal diagonal and zeros elsewhere.

In the further analysis it is convenient to define pseudo-compositions $(\hat{x})$ by

$$(\hat{x}) = [E]^{-1}(x);\ (\hat{x}_0) = [E]^{-1}(x_0);\ (\hat{x}_\mathrm{I}) = [E]^{-1}(x_\mathrm{I}). \tag{21}$$

By pre-multiplying eq. (15) by $[E]^{-1}$ we obtain a set of two linear *uncoupled* differential equations in the pseudo-composition space

$$\frac{\mathrm{d}\hat{x}_i}{\mathrm{d}t} = \lambda_i(\hat{x}_{i\mathrm{I}} - \hat{x}_i);\quad i = 1, 2 \tag{22}$$

subject to the initial condition

$$t = 0,\ \hat{x}_i = \hat{x}_{i0};\ \Delta\hat{x}_{i0} = \hat{x}_{i\mathrm{I}} - \hat{x}_{i0};\quad i = 1, 2. \tag{23}$$

The two differential eqs (22) can be solved independently giving the transient trajectory in pseudo-space

$$\hat{x}_{i\mathrm{I}} - \hat{x}_i = \exp(-\lambda_i t)\,\Delta\hat{x}_{i0};\quad i = 1, 2 \tag{24}$$

or, expressed in matrix notation:

$$(\hat{x}_\mathrm{I} - \hat{x}) = \begin{pmatrix} \exp(-\lambda_1 t)\,\Delta\hat{x}_{10} \\ \exp(-\lambda_2 t)\Delta\hat{x}_{20} \end{pmatrix}. \tag{25}$$

Premultiplying eq. (25) by $[E] = [(e_1)\ (e_2)]$ we obtain the transient composition trajectories in *real* composition space

$$(x_\mathrm{I} - x) = \exp(-\lambda_1 t)\Delta\hat{x}_{10}(e_1) + \exp(-\lambda_2 t)\Delta\hat{x}_{20}(e_2) \tag{26}$$

which relation is most useful in analysing the experimental data.

On examining eq. (26) we note that if the starting composition in the particular phase is so chosen that either $\Delta\hat{x}_{10}$ or $\Delta\hat{x}_{20}$ vanishes then the equilibration trajectory must be rectilinear, parallel to the eigenvectors (e_2) and (e_1) in the two respective cases. But since the elements of $[K]$ are not known in advance, the matrix $[E]$ is unknown and it is not possible to make the choice of the initial state such that one of the $\Delta \hat{x}_{i0}$ vanishes. However, the choice of the initial state leading to a rectilinear equilibration trajectory *can* be made on purely *physical* grounds. Consider the conditions depicted as Run A in Fig. 3. The acetone rich phase is chosen initially to have the composition A_0 corresponding to the saturation point A_I on the binodal curve. The initial composition in the glycerol-rich phase is chosen such that the point G_0 lies on the extension of the tie-line through A_I. Since the mixture composition also lies on the tie-line, we must conclude purely from material balance considerations that the trajectory in the glycerol phase must lie on the straight line $G_0 - G_I$; any deviations from rectilinearity will violate the mass balance constraints for the individual species. The crosses on the straight line $G_0 - G_I$ correspond to the experimentally determined compositions for this type of experiment, lending confirmation to our fundamental expectations. By an exactly parallel reasoning, we must conclude that if the glycerol-rich phase is chosen to have the initial saturation composition G_I and the initial acetone-rich phase composition A_0 corresponds to a position on the extension of the tie-line through G_I, then the equilibration trajectory $A_0 - A_I$ must be rectilinear. This was indeed experimentally confirmed as evidenced by the crosses (measured data) on the line $A_0 - A_I$ for Run B in Fig. 3.

A more stringent test of eq. (26) is to determine the eigenvalue corresponding to the straight line trajectory using eq. (26). If the two key assumptions made in the derivation of eq. (26), i.e. constancy of $[K]$ and of x_{iI}, are satisfactory, then a plot of $-\ln(x_{iI} - x_i)$ vs t should yield a straight line. The two plots for Runs A and B are shown in Fig. 4. In the glycerol-rich phase λ_1'' is calculated to be 0.19 h^{-1} and the agreement with the theory is good for this Run A. For Run B the agreement with theory is not so good. This is because during the equilibration process the viscosity of the acetone-rich phase (with no glycerol in the starting composition A_0) increases substantially and the assumption of constant $[K]$ is severely tested. The limitations in the assumption of constant $[K]$ in the acetone-rich phase will also be raised again in a further connection. Even so, we consider the value of $\lambda_1' = 0.287\ \text{h}^{-1}$ to be a fair representation of the trajectory $A_0 - A_I$ of Run B.

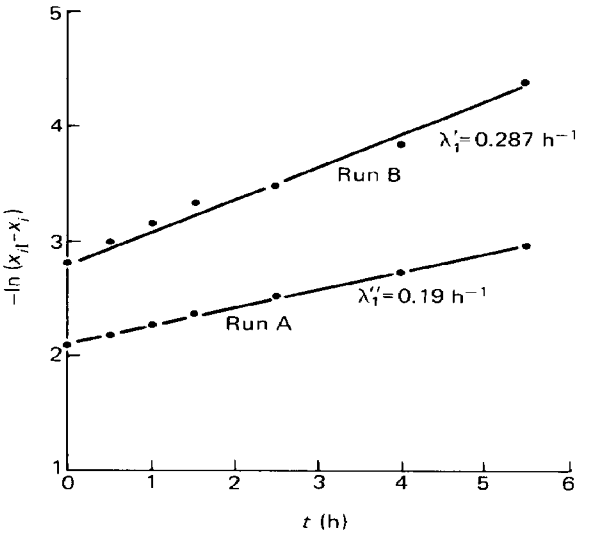

Fig. 4. Plot of $-\ln(x_{1I} - x_1)$ vs time for Runs A and B. λ_1 is the eigenvalue (rate constant) for the equilibration process.

Clearly, experiments of the types Run A and B, though confirming our expectations of rectilinear trajectory, yield only limited information on the structure of $[K]$. On the basis of these experiments it is not possible to conclude whether the off-diagonal elements of $[K]$ are significantly non-zero or not. To gain better insight into $[K]$ it is necessary to perform an experiment of the type shown in Fig. 5, with both

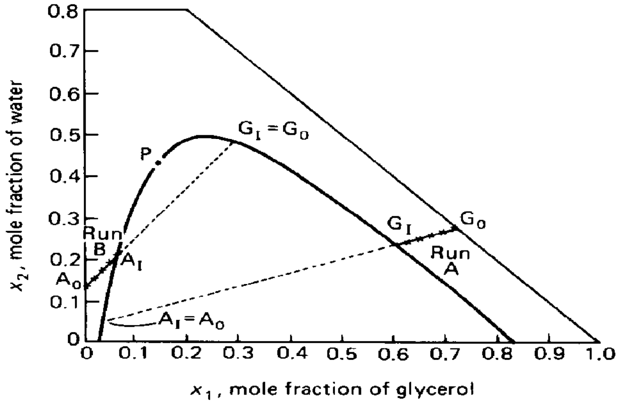

Fig. 3. Rectilinear trajectories obtained experimentally for glycerol–water – acetone. For Run A, the acetone-rich phase remains saturated throughout the experiment and for Run B, the glycerol-rich remains at its saturation point on the binodal throughout the experiment.

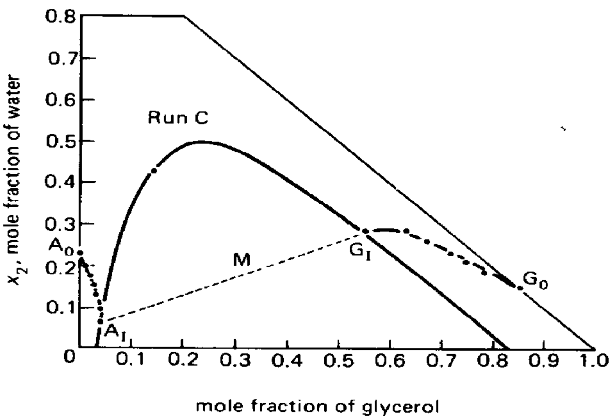

Fig. 5. Experimentally observed equilibration trajectories for Run C with two unsaturated phase compositions A_0 and G_0 as initial points. M is the mixture point. $A_I - G_I$ represents the tie-line through M.

the initial compositions G_0 and A_0 being unsaturated and not lying on a tie-line. For the conditions depicted in Fig. 5, highly curvilinear trajectories were obtained experimentally. Interestingly, the approach towards G_I in the glycerol-rich phase is concave to the binodal curve, while the corresponding approach to A_I is convex. Furthermore, towards the last stages of equilibration to G_I, the approach was found to be collinear with the tie-line $A_I - G_I$. On the other hand, in the acetone-rich phase the approach to A_I, towards the latter stages of the equilibration process, was along the binodal curve, as shown in Fig. 5.

First let us examine whether a pseudo-binary for mass transfer will be adequate to describe the composition trajectories measured for Run C. We shall assume that each component in the ternary mixture relaxes to the equilibrium with its own characteristic rate constant, $K_{i,\text{eff}}$. Then the composition trajectories are

$$(x_{iI} - x_i) = \exp(-K_{i,\text{eff}}t)\,\Delta x_{i0}; \quad i = 1, 2, 3. \tag{27}$$

Since the component driving forces add to zero we can eliminate the Δx_{30} to obtain

$$[\exp(-K_{1,\text{eff}}t) - \exp(-K_{3,\text{eff}})]\,\Delta x_{10} + [\exp(-K_{2,\text{eff}}t) - \exp(-K_{3,\text{eff}}t)]\,\Delta x_{20} = 0 \tag{28}$$

which equality must hold for all combinations of Δx_{10} and Δx_{20}, which are each independently variable. So the only solution possible to eq. (28) is when the pseudo-binary rate constants are equal to one another:

$$K_{1,\text{eff}} = K_{2,\text{eff}} = K_{3,\text{eff}} = K \tag{29}$$

or in other words the matrix $[K]$ must reduce to a scalar, K, times the identity matrix $[I]$. When this happens the composition trajectories given by eq. (27) must be rectilinear. Since the observed trajectories are highly curvilinear we must reject the premise that a pseudo-binary mass transfer formulation can be used to describe the interphase mass transfer process. Another, even more persuasive, argument to support this conclusion arises by a visual examination of the trajectory in the glycerol-rich phase in Fig. 5. A tangent to the initial trajectory passing through G_0 will miss the binodal curve completely showing that a simple relation of the form of eq. (27) cannot be valid. Put another way, accepting eq. (27) implies that the composition trajectories must always be directed towards the equilibrium point, which is certainly not the case for Run C.

On the basis of the arguments given above we must accept that the trajectories obtained for Run C can only be explained if we allow for off-diagonal elements in $[K]$. When this is the case the two eigenvalues λ_1 and λ_2 will be different from each other; both will however be positive and real (see Appendix A for proof of this). Without loss of generality we take λ_1 to be the dominant eigenvalue and so $\exp(-\lambda_1 t)$ will decay much faster than $\exp(-\lambda_2 t)$. From equation (26) we must conclude therefore that in the initial stages the composition trajectory must lie along (e_1). The first eigenvector can, therefore, be determined by drawing a tangent to the observed trajectory at the initial point. Following this procedure we determine the two eigenvectors (e'_1) and (e''_1) to be

$$(e'_1) = \begin{pmatrix} -0.45 \\ 1 \end{pmatrix}; \quad (e''_1) = \begin{pmatrix} -1.4 \\ 1 \end{pmatrix} \tag{30}$$

in the acetone-rich and glycerol-rich phases respectively.

Towards the end of the equilibration process, $\exp(-\lambda_1 t)$ will have decayed to zero and the final trajectory must lie along (e_2); see eq. (26). In the glycerol-rich phase, the approach to G_I is observed to be collinear with the tie-line $A_I - G_I$, as seen in Fig. 5. The second eigenvector (e''_2) can then be taken as the tie-line $A_I - G_I$ and so

$$(e''_2) = \begin{pmatrix} 2.3 \\ 1 \end{pmatrix}. \tag{31}$$

In the acetone-rich phase, the final trajectory is seen to hug the binodal curve and we take (e'_2) to be the tangent to the binodal curve at A_I, giving

$$(e'_2) = \begin{pmatrix} 0.13 \\ 1 \end{pmatrix}. \tag{32}$$

With the knowledge of these eigenvectors we can construct the modal matrix $[E]$ in each phase:

$$[E'] = \begin{bmatrix} -0.45 & 0.13 \\ 1 & 1 \end{bmatrix}; \quad [E''] = \begin{bmatrix} -1.4 & 2.3 \\ 1 & 1 \end{bmatrix} \tag{33}$$

which now allow us to determine the pseudo-composition trajectories from the measured data by use of eq. (21). It follows from eq. (24) that a plot of $-\ln(\hat{x}_{iI} - \hat{x}_i)$ vs t should yield a straight line whose slope can be identified with λ_i. Figure 6 shows the plots

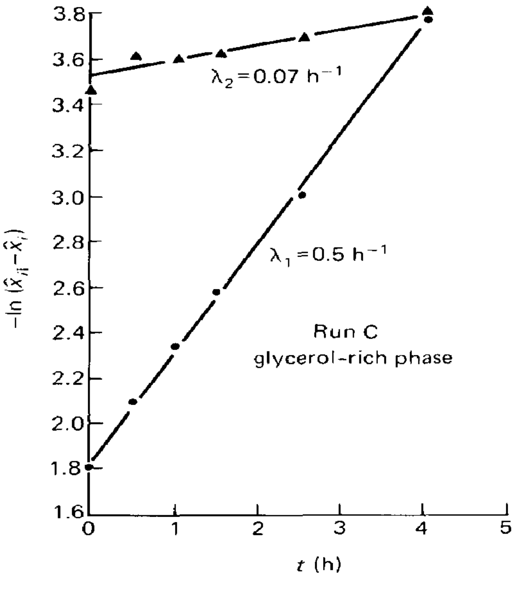

Fig. 6. Plots of $-\ln(\hat{x}_{iI} - \hat{x}_i)$ vs t for Run C in the glycerol-rich phase.

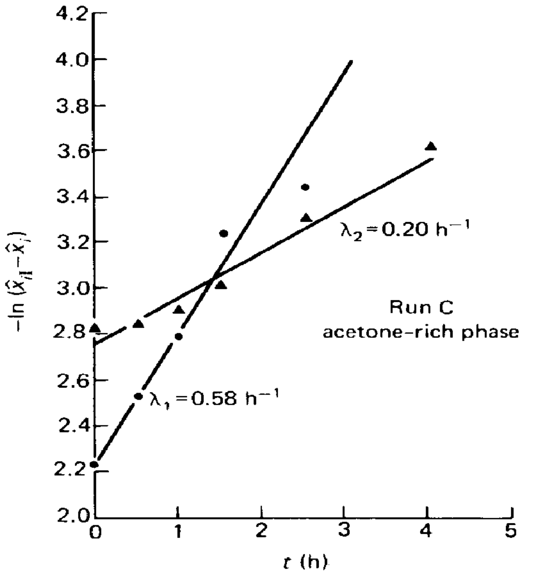

Fig. 7. Plots of $-\ln(\hat{x}_{iI}-\hat{x}_i)$ vs t for Run C in the acetone-rich phase.

for pseudo-components 1 and 2 in the glycerol-rich phase. Reasonable agreement with this theoretical expectation is observed and the eigenvalues λ_1'' and λ_2'' are determined to be 0.5 h^{-1} and 0.07 h^{-1} respectively.

The corresponding results for the acetone rich phase are shown in Fig. 7. Due to the very significant viscosity increases in this phase as extraction proceeds, the assumption of constant $[K]$ is severely tested and the agreement with the theoretical prediction (of constant λ_i') is not as good as for the glycerol-rich phase, though still quite reasonable, in our opinion. The two eigenvalues λ_1' and λ_2' are determined to be 0.58 h^{-1} and 0.20 h^{-1} respectively. Having determined the eigenvalues and eigenvectors in either phase, it is now possible to reconstruct $[K]$ from the relation

$$[K] = [E][\lambda][E]^{-1} \tag{34}$$

which procedure yields

$$[K'] = \begin{bmatrix} 0.495 & -0.038 \\ -0.655 & 0.285 \end{bmatrix}; \quad [K''] = \begin{bmatrix} 0.233 & -0.374 \\ -0.116 & 0.337 \end{bmatrix} \tag{35}$$

with the units h^{-1}.

The matrices $[K']$ and $[K'']$ have indeed quite significant off-diagonal elements confirming our expectation for this highly non-ideal system. In Figs 8 and 9 we compare the predictions of the composition trajectories using these coefficients with the measured data in the glycerol-rich and acetone-rich phases respectively. The agreement between the predictions and measurements is extremely good in the glycerol-rich phase (Fig. 8) and somewhat less good in the acetone-rich phase. Even so, the calculated $[K']$ is able to reproduce the essential features of the convexity in the approach to the equilibrium point (Fig. 9).

EQUILIBRATION TRAJECTORY IN THE VICINITY OF THE PLAIT POINT

We now consider some further interesting features of interphase mass transfer processes in the vicinity of the plait point (P in Fig. 2). It is here that the theory of irreversible thermodynamics is indispensible in our analysis of the diffusion processes. At the plait point we have from equilibrium thermodynamic considerations (see Appendix A)

$$|G| = 0 \tag{36}$$

and one of the eigenvalues of the Fickian matrix of diffusion coefficients $[D]$ vanishes at P. Since $[K]$ is related to the $[D]$, we must conclude that one of the eigenvalues of $[K]$ also vanishes at P. Let us take $\lambda_2 = 0$. From eq. (17) we see that $\lambda_1 = K_{11} + K_{22}$ and the two eigenvectors in the region of P take the form

$$(e_1) = \begin{pmatrix} \dfrac{K_{11}}{K_{21}} \\ 1 \end{pmatrix}; \quad (e_2) = \begin{pmatrix} -\dfrac{K_{12}}{K_{11}} \\ 1 \end{pmatrix}. \tag{37}$$

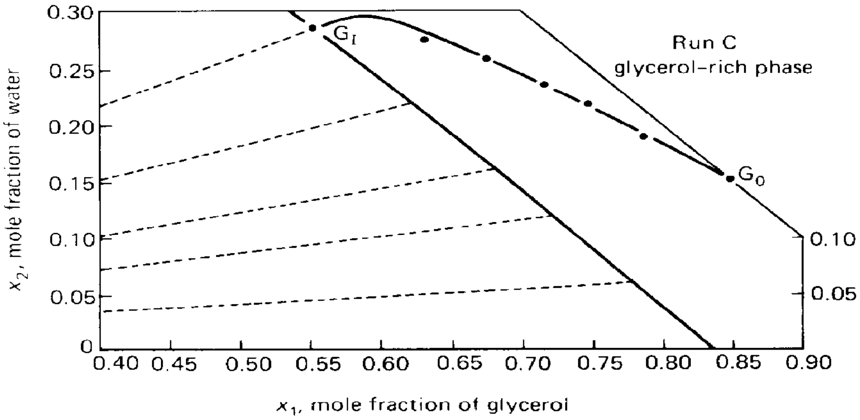

Fig. 8. Comparison of experimentally observed equilibration trajectory with theoretical predictions for Run C in the glycerol-rich phase.

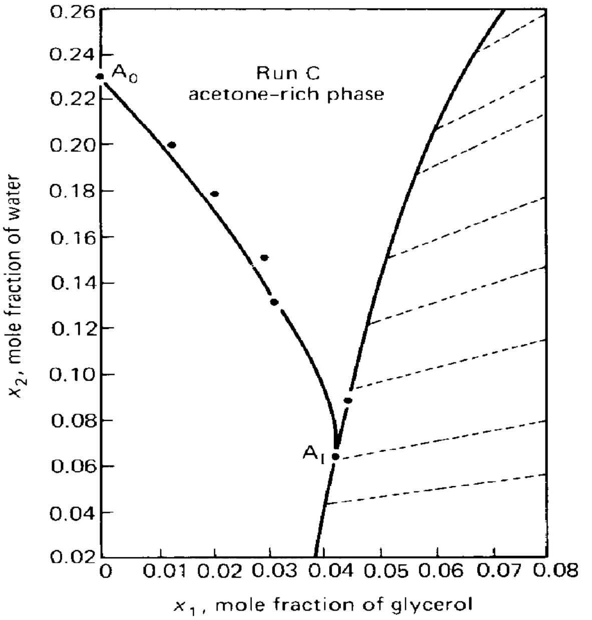

Fig. 9. Comparison of experimentally observed equilibration trajectory with theoretical predictions for Run C in the acetone-rich phase.

The slope of the second eigenvector dx_2/dx_1 is therefore $-K_{11}/K_{12}$. If the interphase mass transfer process can be considered to operate under quasi-steady state conditions, then the film theory model can be used and $[K]$ will be directly proportional to $[D]$. In this case the slope of the second eigenvector will be $-D_{11}/D_{12}$. As shown in Appendix B, the limiting tie-line has the slope $-D_{11}/D_{12}$ and so we conclude that the second eigenvector of $[K]$ in the region of P, i.e. (e_2), is parallel to the limiting tie-line. The final stages of decay of the composition will therefore be parallel to the limiting tie-line. Figure 10 shows diagramatically the actual equilibration run performed with the initial phases lying on the tangent to the binodal curve at the plait point P; these experiments are described in detail in thesis of Louizos [29]. The actual experimental path was indeed found to be linear and the rates of mass transfer lower than in other regions of the ternary diagram. The slowness of the mass transfer can be understood from the fact that the equilibration process is dictated by the smaller of the two eigenvalues and as the critical point is approached, this eigenvalue λ_2 tends to vanish. The above evidence is indicative of the interesting features of interphase mass transfer processes in the region of P and more experiments will be necessary to reveal further features. There appears to be a shortage of experimental mass transfer measurements in the region of the ternary critical point but the available information would suggest that coupling effects are likely to be of great importance here; see for example the experimental data of Vitagliano *et al.* [30] for the system water–chloroform–acetic acid.

CONCLUDING REMARKS

We set out to determine the significance of diffusional coupling effects for interphase mass transfer in non-ideal liquid–liquid systems. Our experimental results on the composition trajectories in a batch extraction cell for the system glycerol–water–acetone have shown that the matrices of volumetric mass transfer coefficients, or equilibration rate constants, $[K']$ and $[K'']$ in the acetone-rich and glycerol-rich phases respectively, have quite significant off-diagonal elements. Also, the experimentally observed trajectories cannot be explained even at a qualitative level by the adoption of pseudo-binary approaches to interphase mass transfer formulations. Rigorous design procedures for extraction equipment must therefore allow for mass transfer coupling effects by incorporating non-diagonal mass transfer coefficient matrices.

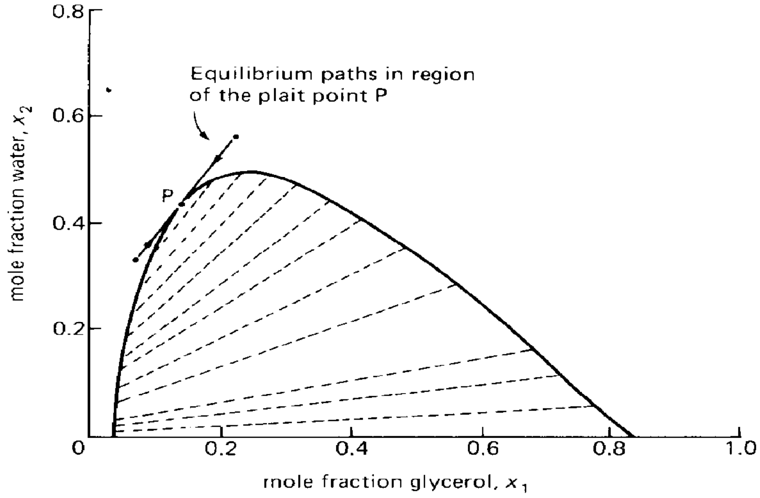

Fig. 10. Experimentally observed equilibration path in the region of the plait point P. Measurements by Louizos [29].

We have also pointed to some interesting mass transfer behaviour in the region of the critical point and presented some evidence to show that the expectations based on the theory of irreversible thermodynamics are borne out in practice. The analysis of the mass transfer process in the region of the critical point shows the indispensibility of a fundamental thermodynamically based approach to mass transport phenomena.

The work reported in this paper could have important consequences in the design of extraction columns because it has a bearing on the interfacial mass transfer rates between the dispersed and continuous phases. In practical systems, the phase hydrodynamics will have the effect of reducing the influence of molecular diffusion coupling; however, close to the interface molecular diffusion will still be controlling and the effects of diffusional coupling will still be significant, as shown by Krishna [32–34] who studied the influence of phase contact time and turbulence levels on diffusional coupling.

The practical consequences of diffusional coupling effects on extraction processes are that the pseudobinary component efficiencies and heights of transfer units will be significantly different from one another and could be unbounded; this has been confirmed for distillation operations [1, 3] and multicomponent extraction measurements in practical contactors will be required to confirm the expectations voiced above.

NOTATION

A_0	initial composition in the acetone-rich phase
A_I	equilibrium composition in the acetone-rich phase
A	interfacial area, m^2
c_t	mixture molar density, kmol m^{-3}
$[D]$	matrix of Fickian diffusivities, $m^2\,s^{-1}$
(e_i)	ith eigenvector of $[K]$
$[E]$	modal matrix of $[K]$
G	molar Gibbs free energy, J $kmol^{-1}$
G_{ij}	second partial derivative of G with respect to composition, J $kmol^{-1}$
G_0	initial composition in the glycerol-rich phase
G_I	equilibrium composition in the glycerol-rich phase
$[H]$	Onsager matrix of coefficients, J $kmol^{-1}\,m^{-2}\,s^{-1}$
$[I]$	identity matrix
$\mathbf{J}_i$	molar diffusion of component i with respect to the molar average mixture velocity, kmol $m^{-2}\,s^{-1}$
(J)	$n-1$ dimensional column matrix of molar diffusion fluxes, kmol $m^{-2}\,s^{-1}$
$[k]$	matrix of mass transfer coefficients, m s^{-1}
$[K]$	matrix of volumetric mass transfer coefficients, or equilibration rate constants, s^{-1} or h^{-1}
$K_{i,\mathrm{eff}}$	pseudo-binary equilibration rate constant, s^{-1} or h^{-1}
M_i	moles of component i in batch cell, kmol
M_t	moles of total mixture in batch cell, kmol
n	number of components in mixture
N_i	molar flux of component i referred to a laboratory fixed coordinate frame of reference
N_t	mixture molar flux relative to a laboratory fixed coordinate frame of reference
s	surface renewal frequency, s^{-1}
t	time, s or h
x_i	mole fraction of component i in the bulk phase
x_{iI}	mole fraction of component i at the interface
x_{i0}	mole fraction of component i at the start of the experiment
$\hat{x}_i$	pseudo-mole fraction of component i
Δx_{i0}	$= x_{iI} - x_{i0}$, initial composition driving force

Greek letters

δ	film thickness, m
λ_i	eigenvalue of $[K]$, s^{-1} or h^{-1}
μ_i	molar chemical potential of component i, J $kmol^{-1}$
σ	rate of entropy production, J $m^{-3}\,s^{-1}\,K^{-1}$
σ_{x_i}	standard deviation of composition determination

Matrix notation

$(\ )$	$n-1$ dimensional column matrix
$[\ ]$	$n-1 \times n-1$ dimensional square matrix
$[\ ]^{-1}$	inverted matrix

Subscripts

I	referring to interface
0	referring to initial composition or condition at $t = 0$

Superscripts

$'$	referring to acetone-rich phase
$''$	referring to glycerol-rich phase
$\hat{}$	pseudo-species or parameter

Vector notation

$\nabla_{T,p}$	gradient operator under isothermal and isobaric conditions
	dot product between two vectors

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APPENDIX A

For diffusion in the absence of external force fields (such as gravitational, electrostatic, magnetic etc.), the rate of entropy production in n-component component mixtures is obtained from the theory of irreversible thermodynamics [5–7] as

$$\sigma = -\frac{1}{T}\sum_{i=1}^{n-1} \mathbf{J}_i \cdot \nabla_{\mathrm{T,p}}(\mu_i - \mu_n) \geqq 0 \qquad \text{(A-1)}$$

where the positive definite condition for σ follows from the second law of thermodynamics. At equilibrium the rate of entropy production vanishes identically.

Due to the Gibbs Duhem relationship, only $n-1$ of the chemical potential gradients $\nabla_{\mathrm{T,p}}\mu_i$ are independent and if we construct a linear constitutive relationship between the $n-1$ independent gradients and the $n-1$ independent fluxes J_i, i.e.

$$\nabla_{\mathrm{T,p}}(\mu - \mu_n) = -\frac{1}{c_t}[H](\mathbf{J}) \qquad \text{(A-2)}$$

then the matrix of these fundamentally defined coefficients is symmetric, i.e.

$$[H] = [H]^T \qquad \text{(A-3)}$$

which is a statement of the Onsager reciprocal relations [5]. A sufficient condition for the entropy production rate σ to be positive definite is that the determinant of the matrix of Onsager coefficients $[H]$ be positive definite, which requires that

$$|H| \geqq 0 \qquad \text{(A-4)}$$

and that the principal cofactors be all positive. This implies that the diagonal elements are all positive

$$H_{ii} \geqq 0 \qquad \text{(A-5)}$$

whereas the off-diagonal elements must satisfy conditions of the form

$$H_{ii}H_{kk} - H_{ik}^2 \geqq 0; \quad i,k = 1,2,\ldots n-1. \quad (i \neq k) \qquad \text{(A-6)}$$

The gradients $\nabla_{\mathrm{T,p}}(\mu_i - \mu_n)$ can be expressed in terms of the mole fraction gradients by the relation

$$\nabla_{\mathrm{T,p}}(\mu - \mu_n) = [G](\nabla x) \qquad \text{(A-7)}$$

where the elements G_{ij} represent the second derivatives of the molar Gibbs free energy G with respect to composition

$$G_{ij} = \frac{\partial^2 G}{\partial x_i \partial x_j} = \frac{\partial(\mu_i - \mu_n)}{\partial x_j} = \frac{\partial(\mu_j - \mu_n)}{\partial x_i} = G_{ji}. \qquad \text{(A-8)}$$

The matrix $[G]$ is symmetric and from thermodynamic stability considerations $[G]$ must be positive definite [28].

Combining eqs (A-2) and (A-7) we obtain

$$(\mathbf{J}) = -c_t[H]^{-1}[G](\nabla x) \qquad \text{(A-9)}$$

and if we define the matrix of Fickian diffusivities $[D]$ by the relation

$$(\mathbf{J}) = -c_t[D](\nabla x) \qquad \text{(A-10)}$$

we see that

$$[D] = [H]^{-1}[G]. \qquad \text{(A-11)}$$

The Fickian matrix $[D]$ is a product of two symmetric, positive definite matrices and from the rules of matrix algebra it follows that the eigenvalues of $[D]$, $\hat{D}_i$ are real and positive definite. Since the structure of $[K]$ is related to the structure of $[D]$, it follows that the eigenvalues of $[K]$ are also real and positive.

Now let us examine the structure of $[D]$. For non-ideal liquid mixtures such as glycerol-water-acetone the matrix $[G]$ will have significant off-diagonal elements. To illustrate this we have calculated G_{ij} for $x_1 = 0.6749$, $x_2 = 0.2588$, $x_3 = 0.0663$ (which represents the glycerol-rich phase compositions measured 2.5 h from the start of the experiment Run C) using the NRTL coefficients fitted to the measured equilibrium data [26]. The values of G_{ij} are:

$$G_{11} = 21.95;\ G_{12} = G_{21} = 18.31; \quad G_{22} = 28.22\ \mathrm{kJ\ mol^{-1}} \qquad \text{(A-12)}$$

demonstrating the strong non-idealities in the system. So, even if the matrix $[H]$ has small off-diagonal elements, the matrix $[D]$, which is the product $[H]^{-1}[G]$ will have significantly large off-diagonal elements. It must be remarked that the matrix $[D]$ is un-symmetric in general.

An interesting property of $[G]$ is that the determinant $|G|$ must vanish at the plait point P, i.e.

$$|G| = 0 \qquad \text{(A-13)}$$

and since it follows from eq. (A-11) that

$$|D| = |G|/|H| \qquad \text{(A-14)}$$

the consequence of eq. (A-13) is that at the plait point

$$|D| = 0 \qquad \text{(A-15)}$$

which means that one of the eigenvalues of $[D]$ must vanish identically at this point. Since $[K]$ is related to $[D]$, it follows that one of the eigenvalues of $[K]$ must also vanish at the plait point P.

APPENDIX B

For equilibrium between the phases ′ and ″ the following condition must be satisfied

$$\mu_i'(x_1', x_2') = \mu_i''(x_1'', x_2''); \quad i = 1, 2, 3 \tag{B-1}$$

and for small variations in either phase we must have

$$\mathrm{d}\mu_i' = \mathrm{d}\mu_i'', \quad i = 1, 2, 3. \tag{B-2}$$

Now, at constant temperature and pressure we have from the Gibbs–Duhem restriction

$$x_1'\,\mathrm{d}\mu_1' + x_2'\,\mathrm{d}\mu_2' + x_3'\,\mathrm{d}\mu_3' = x_1''\,\mathrm{d}\mu_1'' + x_2''\,\mathrm{d}\mu_2'' + x_3''\,\mathrm{d}\mu_3'' \tag{B-3}$$

or writing $x_3 = 1 - x_1 - x_2$ we get

$$x_1'\,\mathrm{d}(\mu_1' - \mu_3') + x_2'\,\mathrm{d}(\mu_2' - \mu_3') = x_1''\,\mathrm{d}(\mu_1'' - \mu_3'') + x_2''\mathrm{d}(\mu_2'' - \mu_3'') \tag{B-4}$$

which can be rearranged to the form

$$\frac{x_2'' - x_2'}{x_1'' - x_1'} = -\frac{\mathrm{d}(\mu_1' - \mu_3')}{\mathrm{d}(\mu_2' - \mu_3')} = -\frac{\mathrm{d}(\mu_1'' - \mu_3'')}{\mathrm{d}(\mu_2'' - \mu_3'')}. \tag{B-5}$$

In the region of the critical point (P in Fig. 2), eq. (B-5) reduces to

$$\frac{\mathrm{d}x_2}{\mathrm{d}x_1} = -\frac{\mathrm{d}(\mu_1 - \mu_3)}{\mathrm{d}(\mu_2 - \mu_3)}. \tag{B-6}$$

Now, from eq. (A-7) we have

$$\mathrm{d}(\mu - \mu_n) = [G]\,\mathrm{d}(x) \tag{B-7}$$

and so eq. (B-6) can be expressed in the region of the critical point as

$$\frac{\mathrm{d}x_2}{\mathrm{d}x_1} = -\frac{G_{11} + G_{12}\dfrac{\mathrm{d}x_2}{\mathrm{d}x_1}}{G_{12} + G_{22}\dfrac{\mathrm{d}x_2}{\mathrm{d}x_1}} \tag{B-8}$$

which represents the slope of the limiting tie-line. Solving the resultant quadratic equation for $\mathrm{d}x_2/\mathrm{d}x_1$ we obtain on invoking the condition that $|G| = 0$ at the critical point:

$$\frac{\mathrm{d}x_2}{\mathrm{d}x_1} = -\frac{G_{12}}{G_{22}} = -\sqrt{\frac{G_{11}}{G_{22}}}. \tag{B-9}$$

Now, using the relationship $[D] = [H]^{-1}[G]$ we see that

$$\frac{D_{21}}{D_{22}} = \frac{D_{11}}{D_{12}} = \sqrt{\frac{G_{11}}{G_{22}}} \tag{B-10}$$

which shows on comparison with eq. (B-9) that the slope of the limiting tie-line is

$$\frac{\mathrm{d}x_2}{\mathrm{d}x_1} = -\frac{D_{21}}{D_{22}} = -\frac{D_{11}}{D_{12}} \tag{B-11}$$

which relation was first derived by Kirkaldy and Purdy [31] using a slightly different approach.