Concentration Gradients in Supersaturated Solutions: a Thermodynamic Analysis

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The development of a concentration gradient along the vertical axis of a column of quiescent solution is explained within the framework of nonequilibrium thermodynamics. The formulae derived enabled us to determine explicitly the concentration difference between two vertical levels in a liquid column and specific conditions under which the concentration profile is at equilibrium. The concept of solute cluster formation in a supersaturated solution is consistent with the presented theory although the theory itself does not provide any direct or indirect proof of the occurrence of clustering.

Introduction

The development of a concentration gradient in a stagnant supersaturated solution contained in a vertical cylinder was first observed by Mullin and Leci (1969) using citric acid solutions. Their observation has since been confirmed for supersaturated solutions of sucrose (Allen et al., 1972, 1973) and several inorganic substances (Larson and Garside, 1986; Rusli and Larson, 1987).

It has usually been assumed that such concentration gradients are related to the formation of clusters in supersaturated solutions (Mullin and Leci, 1969). These are assumed to be loose aggregations of solute molecules, perhaps incorporating a significant proportion of solvent. Once the existence of clusters has been assumed, two different arguments have been used to justify the subsequent development of the concentration gradient. The first assumes that the clusters sediment in the gravitational field (Mullin and Leci, 1969; Allen et al., 1972, 1973). However, a simple calculation shows (Larson and Garside, 1986) that with any reasonable estimate of cluster size, such sedimentation cannot occur over the time scale of the observations. The second argument links thermodynamic developments with concepts of solution structure (Larson and Garside, 1986). This is a somewhat unrigorous treatment since thermodynamic developments should not presuppose any structural details of the system to which they are applied.

The object of this present contribution is to employ the thermodynamics of continua to show that under certain conditions concentration gradients will develop in stagnant supersaturated solutions. The argument developed here is independent of any consideration concerning the presence or absence of clusters in the solution. Consequently the observation that concentration gradients develop in stagnant supersaturated solutions cannot of itself be used to substantiate the existence of clusters.

Thermodynamics of Material Continua

In its usual form chemical thermodynamics is based on expressing the composition of a system in moles; consequently, concentration is expressed in mole fractions, molarities, or molalities. The properties of any system can then conveniently be described by modifying the simple relations valid for ideal behavior using a correction factor characterizing any deviation from ideality. The molar reference scheme also corresponds better to structural theories and statistical thermodynamics. However, when the thermodynamic relations must be combined with other physical laws, many of these advantages vanish. Moreover, the molar concept can be misleading for strongly nonideal systems since it then has little in common with the actual molecular configurations.

An alternative to the molecular concept is the mass concept. The undisputed advantage of such a concept is that its base, mass, is objective and can be measured easily. The formalism that follows is developed in this so-called material continuum, all quantities describing the state of the system being expressed as specific quantities related to unit mass; see Appendix A.

For a binary mixture the Gibbs-Duhem relation, Eq. A10, adopts the form

$$y_1\frac{\partial \hat{Z}_1}{\partial y_2}+y_2\frac{\partial \hat{Z}_2}{\partial y_2}=0 \tag{1}$$

Since $y_1=1-y_2$, Eq. 1 can be transformed into

$$(1-y_1)\frac{\partial \hat{Z}_2}{\partial y_2}=-y_1\frac{\partial \hat{Z}_1}{\partial y_2} \tag{2}$$

or

$$\frac{\partial(\hat{Z}_2-\hat{Z}_1)}{\partial y_2}=\frac{1}{y_1}\frac{\partial \hat{Z}_2}{\partial y_2} \tag{3}$$

According to Eq. A11, Eq. 3 can be recast as

$$\frac{\partial^2 \hat{Z}}{\partial y_2^2}=\frac{\partial(\hat{Z}_2-\hat{Z}_1)}{\partial y_2}=\frac{1}{y_1}\frac{\partial \hat{Z}_2}{\partial y_2} \tag{4}$$

If $\hat{Z}_1$ and $\hat{Z}_2$ are taken to be the chemical potentials of solvent and solute, $\hat{\mu}_1$ and $\hat{\mu}_2$, respectively, then $\hat{Z}$ becomes the Gibbs specific energy of the mixture, $\hat{G}$, and Eq. 4 can be rewritten as

$$\frac{\partial^2 \hat{G}}{\partial y_2^2}=\frac{\partial}{\partial y_2}(\hat{\mu}_2-\hat{\mu}_1)=\frac{1}{y_1}\frac{\partial \hat{\mu}_2}{\partial y_2} \tag{5}$$

Denoting

$$\hat{\nu}_2=\hat{\mu}_2-\hat{\mu}_1 \tag{6}$$

Eq. 5 acquires the form

$$\frac{\partial \hat{\nu}_2}{\partial y_2}=\frac{1}{y_1}\frac{\partial \hat{\mu}_2}{\partial y_2} \tag{7}$$

From the Gibbs equation expressed in mass units for an N-component system

$$d\hat{G}=-\hat{S}dT+\hat{V}dP+\sum_{k=2}^{N}\hat{\nu}_k dy_k \tag{8}$$

the following Maxwell relation can be derived

$$\frac{\partial \hat{\nu}_k}{\partial P}=\frac{\partial \hat{V}}{\partial y_k}=\hat{V}_k-\hat{V}_1 \tag{9}$$

Limit of Thermodynamic Stability

Chemical thermodynamics defines a number of stability conditions of the thermodynamic equilibrium when certain variables, such as pressure and temperature, are held constant. In the present formalism the general formulation of conditions of stability is rather difficult. However, since only the concentration stability—that is, the thermodynamic stability with respect to diffusion—is important in our case, the definition of a relevant subset of conditions is sufficient. From Eq. 8 it follows that

$$\frac{\partial \hat{\nu}_j}{\partial y_k}=\frac{\partial \hat{\nu}_k}{\partial y_j} \quad j,k=2,\ldots,N \tag{10}$$

and therefore the matrix of derivatives $(\partial \hat{\nu}_j/\partial y_k)$ is symmetric. The stability requires that the matrix is positive definite (de Groot and Mazur, 1969), that is,

$$\sum \frac{\partial \hat{\nu}_j}{\partial y_k}dy_j dy_k>0 \tag{11}$$

for $(dy_2,\ldots,dy_N)\neq 0$. The matrix can be diagonalized, that is, off-diagonal elements become zero, and according to Eq. 11 the diagonal elements representing eigenvalues of the matrix must be positive. As the matrix elements $\partial \hat{\nu}_j/\partial y_k$ depend on the thermodynamic state of a system defined by appropriate coordinates the same applies to the eigenvalues. Thus Eq. 11 defines a domain of concentration stability inside the domain of all conceivable values of the coordinates.

By definition, Eq. 11 is satisfied inside the domain of natural states and thus the thermodynamic states outside the domain are considered to be nonexistent unless they are "frozen in" due to their slow rate of transformation under specific conditions. In the case of aqueous solutions of low viscosity any such hindrance arising from kinetic factors is highly improbable. If a solution reaches its stability limit its actual state has to transform into another state that is stable under the given conditions. The processes taking place in a system at its stability limit are not considered in the present contribution.

For a binary solution the conditions of thermodynamic stability and the stability limit respectively become

$$\varphi=\frac{\partial \hat{\nu}_2}{\partial y_2}>0 \text{ and } \varphi=\frac{\partial \hat{\nu}_2}{\partial y_2}=0 \tag{12}$$

The function $\hat{\nu}_2(y_2)$ and the stability limit are shown in Figure 1b for a system where species 1 and 2 have been selected in such a way that the stability limit is approached when y_2 increases. Equation 12 is invariant with respect to the choice of molecular species; hence let y_1 and y_2 represent the mass fraction of solvent and unsolvated solute, respectively.

For illustration purposes, a point corresponding to the saturated solution of concentration $y_{2,eq}$ is arbitrarily situated in Figure 1. It can be seen that in a thermodynamic sense the saturation point is always at some distance from the stability limit $y_{2,\infty}$. Thus, a solution of concentration $y_2<y_{2,eq}$ is undersaturated, $y_2=y_{2,eq}$ corresponds to saturation, and $y_2>y_{2,eq}$ is supersaturated. The region between $y_{2,eq}$ and $y_{2,\infty}$ is called the metastable region the width of which, $y_{2,\infty}-y_{2,eq}$, does not in

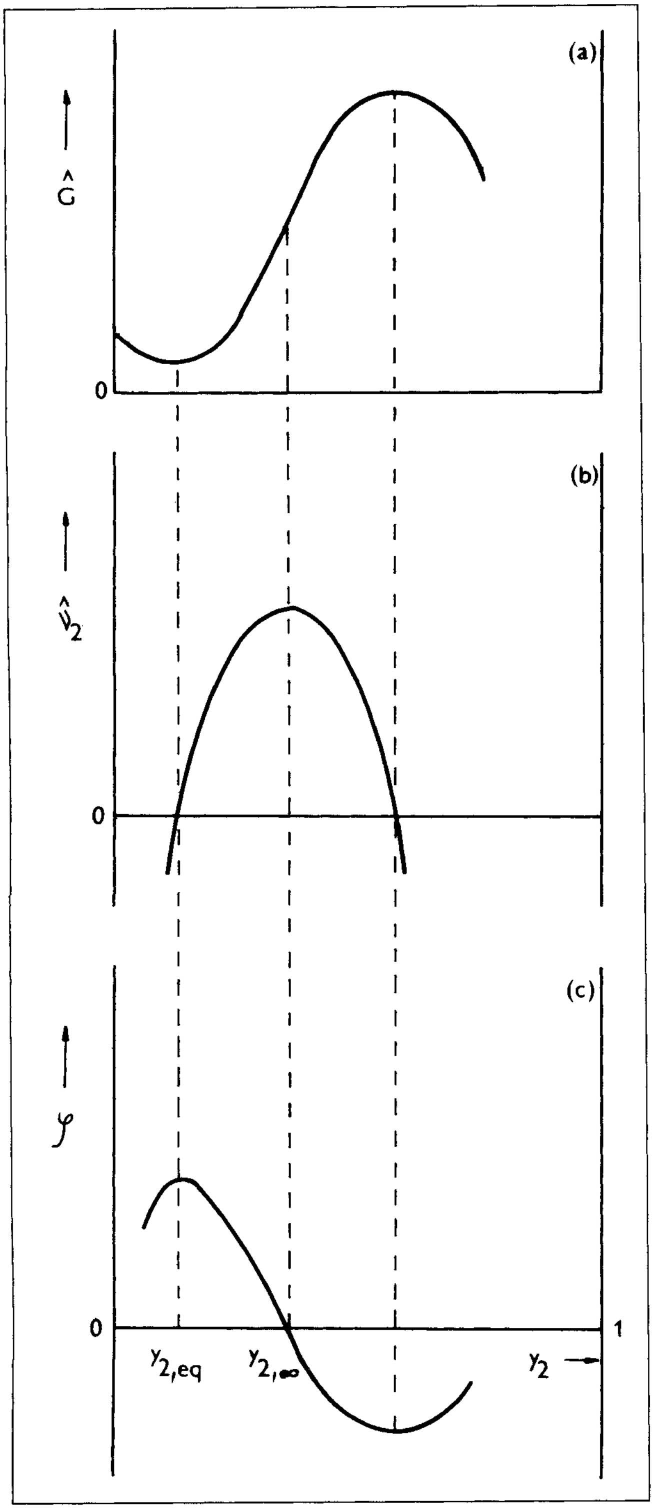

Figure 1. Binary system concentration.

a. Dependence of $\hat G$ on system composition
b. First derivative of the curve: $\hat v_2$ as a function of composition
c. Second derivative of the curve: φ as a function of composition

general coincide with the metastable zone as conventionally used in crystallization (Nývlt et al., 1985).

For the system considered here, the Gibbs specific energy changes with composition according to the curve shown in Figure 1a. The first derivative of this curve, Figure 1b, then represents the dependence of $\hat v_2$ on y_2 while the second derivative, Figure 1c, corresponds to the function $\varphi(y_2)$. According to Eq. 12 the system under consideration is thermodynamically stable when $\varphi > 0$, that is, in the region where $y_2 < y_{2,\infty}$ and the stability limit defined as $\varphi = 0$ is situated at $y_2 = y_{2,\infty}$. Beyond this point the homogeneous system must spontaneously decompose into two different phases with different densities—the so-called spinodal decomposition—unless kinetic factors prevent this. Thus in the region $y_2 \leq y_{2,\infty}$ only diffusion of solute in the system can be responsible for the development of any concentration gradient, whereas in the region $y_2 > y_{2,\infty}$ the sedimentation of a newly formed phase must be responsible. This phase need not be the thermodynamically stable crystalline phase, but may be a metastable glasslike phase.

In the subsequent discussion we consider only the region $y_2 \leq y_{2,\infty}$ and ignore consideration of the region where spinodal decomposition of the system takes place.

In a binary solution at constant temperature within which a concentration and pressure gradient exists, a flux of matter j_2 is established due to existing gradients. After some time has elapsed, theoretically after an infinite time, an equilibrium characterized by $j_2 = 0$ is attained. The distribution of concentration in a system at such an equilibrium satisfies the relation

$$\nabla y_2 = -\frac{1}{\left(\dfrac{\partial \hat v_2}{\partial y_2}\right)}\frac{\partial \hat V}{\partial y_2}\rho g \qquad (13)$$

see Appendix B.

To describe a binary solution placed in a vertical cylinder with constant cross section forming a liquid column of depth H with the zero position corresponding to the liquid surface, Eq. 13 takes the form

$$\frac{dy_2}{dz} = -\frac{1}{\varphi}\epsilon\rho g \qquad (14)$$

where

$$\epsilon = \frac{\partial \hat V}{\partial y_2} = -\frac{1}{\rho^2}\frac{\partial \rho}{\partial y_2} = \hat V_2 - \hat V_1 \qquad (15)$$

Thus, when $\epsilon \neq 0$ a varying concentration along the height of the vertical cylinder, (along the z axis), henceforth referred to as the concentration profile, is established at equilibrium. Under ordinary conditions, such as when the cylinder is in the earth's gravitational field, the concentration change will be negligible unless φ acquires a rather small value, as it would in the vicinity of the stability limit. Under such conditions the change of concentration along the axis, dy_2/dz, can become significant.

Development of a Concentration Profile

We now evaluate the equilibrium concentration profile in a binary solution on the basis of Eq. 14. An approximation for the dependence of φ on y_2 is obtained if $\hat v_2$ is expanded in the vicinity of the stability limit $y_{2,\infty}$ using the Taylor series. Thus

$$\hat v_2(y_2) = \hat v_2(y_{2,\infty}) + Ox(y_2 - y_{2,\infty}) - \frac{1}{2}K^2(y_2 - y_{2,\infty})^2 + \dots \qquad (16)$$

K^2 denotes the numerical value of the second derivative taken as a negative quantity. Since the second derivative is negative as the stability limit $\hat{v}_2(y_2)$ goes through a maximum, the negative sign has to be introduced into Eq. 16. Thus

$$\varphi(y_2) \doteq K^2(y_{2,\infty} - y_2) \tag{17}$$

Denoting the departure of the actual state of a system from the stability limit as

$$v = (y_{2,\infty} - y_2) \tag{18}$$

and using Eq. 17, Eq. 14 becomes

$$K^2 v dv = \epsilon_0 \rho_0 g dz \tag{19}$$

where ϵ and ρ are taken as constants equal to their initial values ϵ_0 and ρ_0, respectively.

Assuming that the possible changes of the initial height of a liquid column resulting from the establishment of the equilibrium concentration and therefore also the density profile are negligible, the following relation holds:

$$\int_0^H \rho y_2 dz = \rho_0 y_{2,0} H \tag{20}$$

Written in terms of v and with $\rho = \rho_0$ this becomes

$$\int_0^H v dz = v_0 H \tag{21}$$

where $v_0 = (y_{2,\infty} - y_{2,0})$ denotes the initial departure from the stability limit. The general solution of Eq. 19 is

$$v^2 = [v(H)]^2 - \beta(z - H) \quad (v > 0) \tag{22}$$

Here

$$\beta = -\frac{2\epsilon_0 \rho_0 g}{K^2} \tag{23}$$

represents the material property of the system under consideration when in its initial state.

Combining Eqs. 20 and 21, subsequent integration yields

$$\frac{1}{\beta} \int_{[v(H)]^2}^{[v(H)]^2 + \beta H} \xi^{1/2} d\xi = v_0 H \tag{24}$$

It follows that

$$(x + \beta H)^{3/2} - x^{3/2} = \frac{3}{2} \beta v_0 H \tag{25}$$

where

$$x = [v(H)]^2 > 0 \tag{26}$$

is the required unknown.

If a solution of Eq. 25 exists, three different cases may arise:

1. If $\epsilon_0 = 0$ then $\beta = 0$; hence v remains constant, Eq. 22, and is equal to v_0 Eq. 21; a concentration profile does not therefore develop.
2. If $\epsilon_0 < 0$, that is, if solute is the denser component, $\beta > 0$. Then the solution of Eq. 25 is unique and can be found numerically for a given case. Substituting such a solution into Eq. 22 yields

$$v^2 = x + \beta(H - z) \quad (v > 0) \tag{27}$$

This equation shows that v decreases with increasing z and thus the concentration increases toward the bottom of the solution column.

3. If $\epsilon_0 > 0$, that is, if solute is the less dense component, then $\beta < 0$. For $z = 0$, $x' = [v(0)]^2 > 0$ and Eq. 27 provides $x' = x + \beta H$, while Eq. 25 becomes ($|\beta| = -\beta$)

$$(x' + |\beta| H)^{3/2} - x'^{3/2} = \frac{3}{2} |\beta| v_0 H \tag{28}$$

This equation is identical to Eq. (25), having the solution

$$v^2 = x' + |\beta| z \quad (v > 0) \tag{29}$$

It follows from Eq. 29 that v increases with increasing z and hence the concentration increases toward the top of the solution column.

A solution of Eq. 25 may not exist, its existence depending on the numerical values of β, H, and v_0. The limiting condition beyond which a solution does not exist, given when either x or x' equals zero, occurs when

$$(|\beta| H)^{3/2} = \frac{3}{2} |\beta| v_0 H \tag{30}$$

Therefore, if for a given H

$$v_0 < \frac{2}{3} (|\beta| H)^{1/2} \tag{31}$$

or for a given v_0

$$H > \frac{1}{|\beta|} \left(\frac{3}{2} v_0 \right)^2 \tag{32}$$

Eqs. 25 and 28 respectively have no solution and an equilibrium concentration profile is never established. The values of v_0 or H satisfying Eq. 30 can respectively be regarded as the critical departure from the stability limit and the critical depth of a liquid column. When they are exceeded, a new phase will be formed before equilibrium is attained, preferably in a region where v has its smallest value: for $\epsilon_0 < 0$ near the bottom and for $\epsilon_0 > 0$ near the top of the column.

A new phase may be formed even under conditions when v_0 is higher or H lower than the respective critical value if, for example, the kinetics of the new phase formation are fast, but the stability limit can never be exceeded except under exceptionally slow kinetic conditions, as may occur in glass transformations.

Formation of Clusters

In the preceding section the development of a concentration gradient in a quiescent supersaturated solution was predicted on the basis of the phenomenological equilibrium thermodynamics without invoking the concept of clustering. Such structural concepts are beyond thermodynamics and must be avoided when thermodynamics is applied rigorously. We will, however, examine the plausibility of the clustering concept in the light of the thermodynamic treatment of the phenomenon under consideration.

We consider a binary solution at constant temperature. If the actual value of φ is not too small-that is, if the system is rather distant from the stability limit defined by Eq. 12—any concentration fluctuation once developed will tend to be obliterated. This is because the increasing differences in concentration y_2 established in a certain direction as a result of a fluctuation increase $\nabla \hat{v}_2$ in the same direction. Since this represents the driving force for diffusion, Eq. B1, the solute flux j_2 increases in the opposite direction. The established flux therefore decreases the concentration difference and diminishes the fluctuation. Consequently, the solute distribution throughout the system tends to be uniform. When φ decreases, such obliterating tendencies decrease and become increasingly ineffective. Then localized regions of higher and lower solute concentration develop in a system and, on the microscopic scale, the solute distribution is nonuniform throughout the system. A new state of molecular configuration or aggregation is thus established and regions of higher solute concentration can be regarded as clusters.

Obviously the idea of clustering in a system near the stability limit, and thus in a supersaturated solution, does not contradict the concepts of thermodynamics. In fact, clustering can be predicted on the basis of nonequilibrium thermodynamics when applied to processes that may take place in a supersaturated solution. The formation of clusters in a supersaturated solution therefore appears to be a plausible concept.

Although the concept of clustering is consistent with thermodynamics, thermodynamics does not provide any direct or indirect proof of its occurrence.

Discussion

By considering the phenomenological thermodynamics of continua it has been shown that a concentration gradient always develops in a vertical column of a supersaturated solution under the influence of a gravitational field when the difference in the partial specific volumes of solute and solvent, ϵ_0, is not zero. However, for the gradient to become detectable both ϵ_0 should be nonnegligible and φ defined by Eq. 12 must acquire a rather small value. This may happen especially if, let us say, a glasslike second phase occurs which is metastable with reference to the crystalline phase, and, from a physical point of view, differs little from a (saturated) solution. If thus both ϵ_0 is nonnegligible and φ is small and, in addition, the initial solution concentration is lower, or conversely the height of the solution column is smaller, than the respective critical values given by Eqs. 31 and 32, an equilibrium concentration profile will be established after a certain relatively long time period.

The concentration gradient develops despite the fact that the diffusivity at the stability limit becomes zero. The diffusivity in a binary solution is defined as

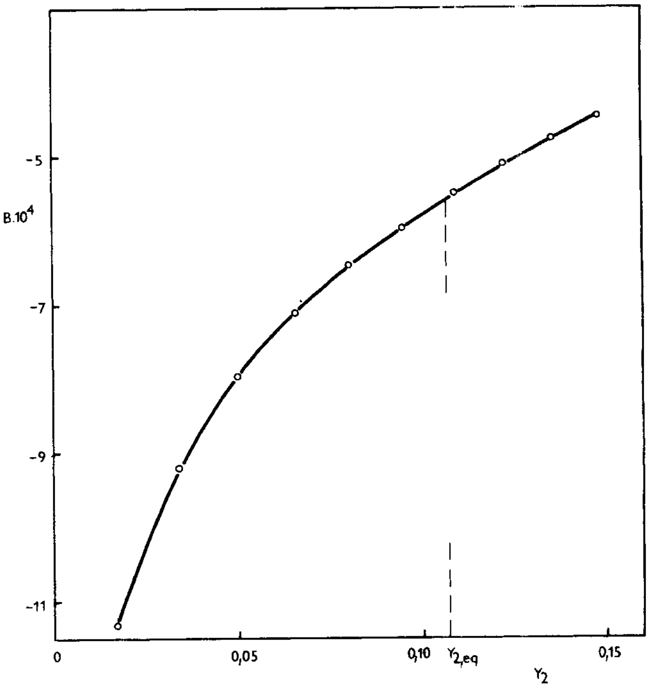

Figure 2. *B*, defined by Eq. 35, as a function of concentration y_2 for K_2SO_4 solutions.

$$D=\frac{L_{22}}{T}\frac{\partial \hat{v}_2}{\partial y_2} \tag{33}$$

where $L_{22} \neq 0$. At the stability limit $\partial \hat{v}_2/\partial y_2 = 0$, Eq. 12, and thus $D=0$, as has been verified experimentally (Chang and Myerson, 1984). However, since $\partial \hat{v}_2/\partial P$ and ∇P under such conditions are still nonzero quantities, then according to Eq. B6 $\nabla \hat{v}_2 \neq 0$, that is, the concentration gradient develops in the solution as a result of diffusion driven by the pressure gradient.

The theory presented above can be compared with experimental results for supersaturated potassium sulfate solutions for which the concentration gradient has been determined and the appropriate thermodynamic function has been extrapolated into the supersaturated region.

Substituting Eq. A1 into Eq. 6 and combining the result with the definition of chemical potential:

$$\mu = \mu^0 + RT \ln a \tag{34}$$

yields after rearranging:

$$B = \hat{v}_2 - \left(\frac{\mu_2^0}{M_2} - \frac{\mu_1^0}{M_1}\right) = RT \ln \frac{a_2^{1/M_2}}{a_1^{1/M_1}} \tag{35}$$

Introduction of the quantity B that is directly related to $\hat{v}_2$ is advantageous since it consists only of measurable quantities.

Using data reported by Lenzi et al. (1975), activities of water in K_2SO_4 solution of concentration up to 2.2 mol/kg water have been recalculated as solute activity coefficients using the Gibbs-Duhem relation and the quantity B numerically evaluated for various concentrations. The resulting values of B plotted as a function of concentration in Figure 2 demonstrate that the condition of stability, Eq. 12, is satisfied over the region for which measurements are available. Figure 2 also demonstrates that φ decreases with increasing concentration so that the system is moving toward the stability limit.

Combining Eqs. 12, C5, and C13 (Appendix C) with the definition of y_1 yields

$$\varphi = \frac{(x_1M_1 + x_2M_2)^2}{M_1M_2^2}(1 + mM_2)\nu RT \frac{\partial \ln a_2^{1/\nu}}{\partial x_2} \tag{36}$$

where mole fractions are based on the convention $x_1 + x_2 = 1$. Inserting the numerical values of individual quantities into Eq. 36

$M_1 = 18.01$
$M_2 = 174.25\ \mathrm{kg \cdot kmol^{-1}}$
$R = 8.31 \times 10^3\ \mathrm{J \cdot K^{-1} \cdot kmol^{-1}}$
$m = 7.9 \times 10^{-4}\ \mathrm{kmol \cdot kg^{-1}}$
$T = 298\ \mathrm{K}$
$\nu = 3$
$(\partial \ln a_2^{1/\nu}/\partial x_2)_{y_2=0.12} \sim 43$ as inferred from the data given by Söhnel and Garside (1979)

yields $\varphi = 2.61 \times 10^5\ \mathrm{m^2 \cdot s^{-2}}$. The density of K_2SO_4 solution can be correlated by (Söhnel and Novotny, 1985)

$$\rho = 996.78 + 826.59y_2 - 37.878y_2^2 \tag{37}$$

from which a solution of $y_2 = 0.120$ has the density $\rho = 1{,}095\ \mathrm{kg \cdot m^{-3}}$ and $(\partial\rho/\partial y_2)_{y_2=0.12} = 817.5\ \mathrm{kg \cdot m^{-3}}$.

Inserting the resulting numerical values of φ, ϵ, and $g = 9.81\ \mathrm{m \cdot s^{-2}}$ into Eq. 14 and integrating between the limits 0 and 0.3 m (the depth of the liquid column used in the respective concentration gradient experiments of Larson and Garside, 1986) results in

$$\Delta y_2 = y_2(\mathrm{bottom}) - y_2(\mathrm{top}) = 8.4 \times 10^{-6} \tag{38}$$

The experimental value of $\Delta y_2 = 1.4 \times 10^{-4}$ was determined at 303 K for a K_2SO_4 solution with $y_2 = 0.120$, that is, a concentration of $7.9 \times 10^{-4}\ \mathrm{kmol \cdot kg^{-1}}$.

The rather large difference between these theoretical (8.4×10^{-6}) and experimental (1.4×10^{-4}) values suggests that either the numerical value of φ has been calculated from incorrect data, or the concentration gradients observed experimentally (Mullin and Leci, 1969; Allen et al., 1972, 1973; Larson and Garside, 1986; Rusli and Larson, 1987) are the result of a different mechanism from that considered here.

To achieve agreement between theory and experiment the value of φ at $y_2 = 0.120$ should equal $1.57 \times 10^4\ \mathrm{m^2 \cdot s^{-2}}$, compared to $2.61 \times 10^5\ \mathrm{m^2 \cdot s^{-2}}$ calculated above. This implies $(\partial \ln a_2^{1/\nu}/\partial x_2)_{y_2=0.12} \sim 2.6$ instead of 43. Such a change would require the activity coefficient, $\gamma_\pm$, to fall more rapidly for increasingly supersaturated solutions than is calculated from the available thermodynamic data. In the present case $\gamma_\pm$ would need to be 0.210 rather than the predicted value of 0.229 for the concentration of supersaturated solution used in the experiments. This is clearly a comparatively small change, particularly when it is recognized that the thermodynamic data in the supersaturated region of potassium sulfate solutions were inferred on the basis of the RWR theory (Reilly et al., 1971) from ternary systems and were not actually measured. Therefore the data employed do not take account of any alteration of the system behavior due to possible clustering in the supersaturated region. Such behavior would indeed result in a more rapid decrease in $\gamma_\pm$ with increasing concentration compared to that calculated. Whether the decrease would be sufficient to satisfy the requirements of the above development is difficult to judge.

On the other hand, the experimentally observed formation of concentration gradients in supersaturated solutions may be caused by spinodal decomposition of some thermodynamically metastable state of the solutions. In such a case the observed phenomenon would result from the rather rapid sedimentation of formed entities of some metastable or amorphous glasslike state and not of diffusion, and thus would be incompatible with the theory developed here.

Which of these two explanations applies to the experiments with supersaturated solutions of potassium sulfate cannot at present be decided.

Conclusions

Development of a concentration gradient in a stagnant supersaturated solution can be predicted based on nonequilibrium thermodynamics. The theory, however, does not provide any proof of solute clustering taking place in a supersaturated solution although this phenomenon is fully compatible with the theory.

Notation

a = activity
B = defined by Eq. 35
D = diffusivity
g = gravitational acceleration
G = Gibbs energy
H = depth of a liquid column
j = flux of matter
K^2 = second derivative of $\hat{\nu}_2$ with respect to y_2
L = matrix element
M = relative molecular mass
m = concentration expressed as molality, mol solute/kg solvent
m_k = mass of the kth component
N = number of components in the mixture
P = pressure
R = gas constant
S = entropy
T = temperature
v = $(y_\infty - y)$ = distance from the stability limit
V = volume
x = mole fraction
y = mass fraction
z = vertical distance
Z = thermodynamic quantity

Greek letters

β = defined by Eq. 23
ϵ = defined by Eq. 15
φ = defined by Eq. 12
μ = chemical potential
μ^0 = standard chemical potential
ν = number of ions in a molecule
$\hat{\nu}$ = defined by Eq. 6
ρ = solution density

Subscripts

1 = solvent
2 = solute
∞ = at the stability limit
eq = equilibrium value
k = kth component
0 = initial value

Other symbols

$\hat{\ }$ = partial specific quantity
$\bar{\ }$ = partial molar quantity

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Appendix A

An N-component homogeneous mixture in a given state of aggregation is characterized by a set of coordinates (T, P, ..., m_k, ...,m_N) where m_k is the mass of the kth component. The total mass of the mixture is $m=\Sigma m_k$.

If Z is an extensive variable, the partial specific quantity $\hat{Z}_k$ is defined by

$$\hat{Z}_k=\frac{\partial Z}{\partial m_k}=\frac{\bar{Z}_k}{M_k} \tag{A1}$$

where $\bar{Z}_k$ is the partial molar quantity. The specific variable $\hat{Z}$ then equals

$$\hat{Z}=\sum_{k=1}^{N} y_k\hat{Z}_k \tag{A2}$$

where y_k is the mass fraction of the kth component, that is,

$$\sum_{k=1}^{N} y_k=1 \tag{A3}$$

and therefore

$$y_1=1-\sum_{k=2}^{N} y_k \tag{A4}$$

Using Eq. A4, Eq. A2 can be rewritten as

$$\hat{Z}=\left(1-\sum_{k=2}^{N} y_k\right)\hat{Z}_1+\sum_{k=2}^{N}\hat{Z}_k y_k \tag{A5}$$

that is,

$$\hat{Z}=\hat{Z}_1+\sum_{k=2}^{N}(\hat{Z}_k-\hat{Z}_1)y_k \tag{A6}$$

By definition, at T, P=constant,

$$(dZ)_{T,P}=\sum_{i=1}^{N}\left(\frac{\partial Z}{\partial m_i}\right)dm_i=\sum_{i=1}^{N}\hat{Z}_i\,dm_i \tag{A7}$$

On the other hand since $Z=\sum_{i=1}^{N} m_i\hat{Z}_i$,

$$(dZ)_{T,P}=\sum_{i=1}^{N}\hat{Z}_i\,dm_i+\sum_{i=1}^{N}m_i(d\hat{Z}_i)_{T,P} \tag{A8}$$

Therefore

$$\sum_{i=1}^{N}m_i(d\hat{Z}_i)_{T,P}=0 \tag{A9}$$

where $\hat{Z}_i$ is independent of the total mass. Thus using variables $(T,P,y_2,...,y_N)$ with $y_i=m_i/m$

$$\sum_{i=1}^{N} y_i\frac{\partial\hat{Z}_i}{\partial y_k}=0 \quad \text{for} \quad k=2,...,N \tag{A10}$$

Applying this to Eq. A6 yields

$$\left(\frac{\partial\hat{Z}}{\partial y_k}\right)_{P,T,y_i\neq y_k}=[\hat{Z}_k-\hat{Z}_1]_{P,T,y_i=y_k} \quad \text{for} \quad k\geq 2 \tag{A11}$$

Equation A11 can be rewritten as

$$\hat{Z}_k=\hat{Z}_1+\left(\frac{\partial\hat{Z}}{\partial y_k}\right)_{P,T,y_i\neq y_k} \tag{A12}$$

Substituting Eq. A12 into Eq. A6 yields

$$\hat{Z}=\hat{Z}_1+\sum_{k=2}^{N}\left(\frac{\partial\hat{Z}}{\partial y_k}\right)_{P,T,y_i\neq y_k}y_k \qquad \text{(A13)}$$

Appendix B

In a system not too far from equilibrium the flux of material due to diffusion can be expressed as

$$j_i=L_{iH}\nabla\left(\frac{1}{T}\right)+\sum_{k=2}^{N}L_{ik}\nabla\left(-\frac{\hat{\nu}_k}{T}\right)\quad i=2,\ldots,N \qquad \text{(B1)}$$

If Eq. B1 is expressed in a molar reference framework, gravitational force terms appear. In the present formulation such terms cancel. The gravitational forces, however, are represented as a pressure gradient under conditions of mechanical equilibrium.

According to the Onsager reciprocity relations, the matrix L of the coefficients in Eq. B1 is symmetric, that is,

$$L_{iH}=L_{Hi}\quad\text{and}\quad L_{ik}=L_{ki}\quad i,k=2,\ldots N \qquad \text{(B2)}$$

The symmetric matrix L is positive definite—all its eigenvalues are positive—and thus all the diagonal terms are positive; thus,

$$L_{HH}>0\quad\text{and}\quad L_{ii}>0 \qquad \text{(B3)}$$

Let the conditions of equilibrium characterized by $j_i=0$ in a material continuum be established for a nonreacting system. The mechanical equilibrium is characterized by

$$\nabla P=\rho g \qquad \text{(B4)}$$

Application of the principles of nonequilibrium thermodynamics to Eq. B1 provides

$$\begin{aligned}&\nabla T=0 &&\text{that is, temperature is constant}\\ &\nabla\hat{\nu}_k=0 &&\text{for } T=\text{constant and } k=2,\ldots,N\end{aligned} \qquad \text{(B5)}$$

since $\nabla\left(\frac{1}{T}\right)=-\frac{1}{T^2}\,(\nabla T)$ and $\nabla\left(-\frac{\hat{\nu}_k}{T}\right)=-\frac{1}{T}\nabla\hat{\nu}_k$ for $T=$constant, respectively. Combining

$$\nabla\hat{\nu}_2=\frac{\partial\hat{\nu}_2}{\partial P}\nabla P+\frac{\partial\hat{\nu}_2}{\partial y_2}\nabla y_2 \qquad \text{(B6)}$$

with Eqs. B4, B5, and 9 and subsequent rearranging yields Eq. 13:

$$\nabla y_2=-\frac{1}{\partial\hat{\nu}_2/\partial y_2}\frac{\partial\hat{V}}{\partial y_2}\rho g$$

Alternatively, Eq. 13 can be derived starting with Eq. B6. In that case, however, proper justification for this expression would be necessary.

Appendix C

The chemical potential of the kth component per unit mass is related to the chemical potential of the same component per unit mole by Eq. A1,

$$\hat{\mu}_k=\frac{\mu_k}{M_k} \qquad \text{(C1)}$$

Thus Eq. 6 can be expressed for a binary mixture as

$$\hat{\nu}_2=\frac{\mu_2}{M_2}-\frac{\mu_1}{M_1} \qquad \text{(C2)}$$

and φ defined by Eq. 12 becomes

$$\varphi=\frac{\partial\hat{\nu}_2}{\partial y_2}=\left(\frac{1}{M_2}\frac{\partial\mu_2}{\partial x_2}-\frac{1}{M_1}\frac{\partial\mu_1}{\partial x_2}\right)\frac{dx_2}{dy_2} \qquad \text{(C3)}$$

Defining the mass fraction of the kth component as

$$y_k=\frac{M_kx_k}{\overline{M}} \qquad \text{(C4)}$$

where the mean molar mass

$$\overline{M}=\sum_{i=1}^{N}M_ix_i \qquad \text{(C5)}$$

we obtain by differentiating Eq. C4

$$dy_k=\frac{M_k}{\overline{M}}dx_k-\frac{M_k}{\overline{M}^2}x_k\sum_{i=1}^{N}M_i\,dx_i \qquad \text{(C6)}$$

Since $\Sigma_{i=1}^{N}x_i=1$, that is, $\Sigma_{i=1}^{N}dx_i=0$, there are only $(N-1)$ independent variables and therefore Eq. C6 can be recast as

$$dy_k=\frac{M_k}{\overline{M}}\left(dx_k-\frac{x_k}{\overline{M}}\sum_{i=2}^{N}(M_i-M_1)dx_i\right) \qquad \text{(C7)}$$

Equation C7 for a binary system, $N=2$, adopts the form

$$dy_2=\frac{M_1M_2}{(\overline{M})^2}dx_2 \qquad \text{(C8)}$$

Substituting Eq. C8 into Eq.C3 provides

$$\varphi=\frac{\partial\hat{\nu}_2}{\partial y_2}=\left(\frac{1}{M_1}\frac{\partial\mu_2}{\partial x_2}-\frac{1}{M_1}\frac{\partial\mu_1}{\partial x_2}\right)\frac{(\overline{M})^2}{M_1M_2} \qquad \text{(C9)}$$

From the Gibbs-Duhem relation, Eq. 1, it follows that

$$\frac{\partial \mu_1}{\partial x_2} = -\frac{x_2}{x_1}\frac{\partial \mu_2}{\partial X_2} \qquad \text{(C10)}$$

and therefore Eq. C9 can be rewritten as

$$\varphi = \frac{\partial \hat{v}_2}{\partial y_2} = \frac{(\overline{M})^2}{M_1 M_2}\left(\frac{1}{M_2} + \frac{x_2}{x_1 M_1}\right)\frac{\partial \mu_2}{\partial X_2} \qquad \text{(C11)}$$

which, after substituting Eq. C5 and

$$y_1 = \frac{M_1 x_1}{\overline{M}} \qquad \text{(C12)}$$

yields

$$\frac{\partial \hat{v}_2}{\partial y_2} = \frac{(\overline{M})^2}{M_1 M_2}\frac{1}{M_2 y_1}\frac{\partial \mu_2}{\partial x_2} \qquad \text{(C13)}$$

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