9.8: Mixtures in Gravitational and Centrifugal Fields

A tall column of a gas mixture in a gravitational field, and a liquid solution in the cell of a spinning centrifuge rotor, are systems with equilibrium states that are nonuniform in pressure and composition. This section derives the ways in which pressure and composition vary spatially within these kinds of systems at equilibrium.

9.8.1 Gas mixture in a gravitational field

Consider a tall column of a gas mixture in an earth-fixed lab frame. Our treatment will parallel that for a tall column of a pure gas in Sec. 8.1.4. We imagine the gas to be divided into many thin slab-shaped phases at different elevations in a rigid container, as in Fig. 8.1. We want to find the equilibrium conditions reached spontaneously when the system is isolated from its surroundings.

The derivation is the same as that in Sec. 9.2.7, with the additional constraint that for each phase α, dV^α is zero in order that each phase stays at a constant elevation. The result is the relation

$$dS = \sum_{\alpha \neq \alpha'} \frac{T^{\alpha'} - T^\alpha}{T^{\alpha'}} \, dS^\alpha + \sum_i \sum_{\alpha \neq \alpha'} \frac{\mu_i^{\alpha'} - \mu_i^\alpha}{T^{\alpha'}} \, dn_i^\alpha \tag{9.8.1}$$

In an equilibrium state, S is at a maximum and dS is zero for an infinitesimal change of any of the independent variables. This requires the coefficient of each term in the sums on the right side of Eq. 9.8.1 to be zero. The equation therefore tells that at equilibrium *the temperature and the chemical potential of each constituent are uniform throughout the gas mixture*. The equation says nothing about the pressure.

Just as the chemical potential of a pure substance at a given elevation is defined in this e-book as the molar Gibbs energy at that elevation (Sec. 8.1.4), the chemical potential of substance i in a mixture at elevation h is the partial molar Gibbs energy at that elevation.

We define the standard potential $\mu_i^\circ(\mathrm{g})$ of component i of the gas mixture as the chemical potential of i under standard state conditions at the reference elevation $h=0$. At this elevation, the chemical potential and fugacity are related by

$$\mu_i(0) = \mu_i^\circ(\mathrm{g}) + RT \ln \frac{f_i(0)}{p^\circ} \tag{9.8.2}$$

If we reversibly raise a small sample of mass m of the gas mixture by an infinitesimal distance dh, without heat and at constant T and V, the fugacity f_i remains constant. The gravitational work during the elevation process is $đw' = mg \, dh$. This work contributes to the internal energy change: $dU = T \, dS - p \, dV + \sum_i \mu_i \, dn_i + mg \, dh$. The total differential of the Gibbs energy of the sample is

$$\begin{aligned} dG &= d(U - TS + pV) \\ &= -S \, dT + V \, dp + \sum_i \mu_i \, dn_i + mg \, dh \end{aligned} \tag{9.8.3}$$

From this total differential, we write the reciprocity relation

$$\left(\frac{\partial \mu_i}{\partial h} \right)_{T,p,\{n_i\}} = \left(\frac{\partial mg}{\partial n_i} \right)_{T,p,n_{j \neq i},h} \tag{9.8.4}$$

With the substitution $m = \sum_i n_i M_i$ in the partial derivative on the right side, the partial derivative becomes $M_i g$. At constant T, p, and composition, therefore, we have $d\mu_i = M_i g \, dh$. Integrating over a finite elevation change from $h = 0$ to $h = h'$, we obtain

$$\mu_i(h') - \mu_i(0) = \int_0^{h'} M_i g \, dh = M_i g h' \tag{9.8.5}$$
$$(f_i(h') = f_i(0))$$

The general relation between μ_i, f_i, and h that agrees with Eqs. 9.8.2 and 9.8.5 is

$$\mu_i(h) = \mu_i^\circ(\mathrm{g}) + RT \ln \frac{f_i(h)}{p^\circ} + M_i g h \tag{9.8.6}$$

In the equilibrium state of the tall column of gas, $\mu_i(h)$ is equal to $\mu_i(0)$. Equation 9.8.6 shows that this is only possible if f_i decreases as h increases. Equating the expressions given by this equation for $\mu_i(h)$ and $\mu_i(0)$, we have

$$\mu_i^\circ(\text{g}) + RT \ln \frac{f_i(h)}{p^\circ} + M_i gh = \mu_i^\circ(\text{g}) + RT \ln \frac{f_i(0)}{p^\circ} \tag{9.8.7}$$

Solving for $f_i(h)$ gives

$$f_i(h) = f_i(0)e^{-M_i gh/RT} \tag{9.8.8}$$
$$\text{(gas mixture at equilibrium)}$$

If the gas is an ideal gas mixture, f_i is the same as the partial pressure p_i:

$$p_i(h) = p_i(0)e^{-M_i gh/RT} \tag{9.8.9}$$
$$\text{(ideal gas mixture at equilibrium)}$$

Equation 9.8.9 shows that each constituent of an ideal gas mixture individually obeys the barometric formula given by Eq. 8.1.13.

The pressure at elevation h is found from $p(h) = \sum_i p_i(h)$. If the constituents have different molar masses, the mole fraction composition changes with elevation. For example, in a binary ideal gas mixture the mole fraction of the constituent with the greater molar mass decreases with increasing elevation, and the mole fraction of the other constituent increases.

9.8.2 Liquid solution in a centrifuge cell

This section derives equilibrium conditions of a dilute binary solution confined to a cell embedded in a spinning centrifuge rotor.

The *system* is the solution. The rotor's angle of rotation with respect to a lab frame is not relevant to the state of the system, so we use a local reference frame fixed in the rotor as shown in Fig. 9.12(a). The values of heat, work, and energy changes measured in this rotating frame are different from those in a lab frame (Sec. G.9 in Appendix G). Nevertheless, the laws of thermodynamics and the relations derived from them are obeyed in the local frame when we measure the heat, work, and state functions in this frame (Sec. G.6).

Note that an equilibrium state can only exist relative to the rotating local frame; an observer fixed in this frame would see no change in the state of the isolated solution over time. While the rotor rotates, however, there is no equilibrium state relative to the lab frame, because the system's position in the frame constantly changes.

We assume the centrifuge rotor rotates about the vertical z axis at a constant angular velocity ω. As shown in Fig. 9.12(a), the elevation of a point within the local frame is given by z and the radial distance from the axis of rotation is given by r.

In the rotating local frame, a body of mass m has exerted on it a centrifugal force $F^{\text{centr}} = m\omega^2 r$ directed horizontally in the outward $+r$ radial direction (Sec. G.9). The gravitational force in this frame, directed in the downward $-z$ direction, is the same as the gravitational force in a lab frame. Because the height of a typical centrifuge cell is usually no greater than about one centimeter, in an equilibrium state the variation of pressure and composition between the top and bottom of the cell at any given distance from the axis of rotation is completely negligible—all the measurable variation is along the radial direction.

> There is also a Coriolis force that vanishes as the body's velocity in the rotating local frame approaches zero. The centrifugal and Coriolis forces are *apparent* or *fictitious* forces, in the sense that they are caused by the acceleration of the rotating frame rather than by interactions between particles. When we treat these forces as if they are real forces, we can use Newton's second law of motion to relate the net force on a body and the body's acceleration in the rotating frame (see Sec. G.6).

To find conditions for equilibrium, we imagine the solution to be divided into many thin curved volume elements at different distances from the axis of rotation as depicted in Fig. 9.12(b). We treat each volume element as a uniform phase held at constant volume so that it is at a constant distance from the axis of rotation. The derivation is the same as the one used in the preceding section to obtain Eq. 9.8.1, and leads to the same conclusion: in an equilibrium state *the temperature and the chemical potential of each substance (solvent and solute) are uniform throughout the solution*.

We find the dependence of pressure on r as follows. Consider one of the thin slab-shaped volume elements of Fig. 9.12(b). The volume element is located at radial position r and its faces are perpendicular to the direction of increasing r. The thickness of the volume element is δr, the surface area of each face is A_s, and the mass of the solution in the volume element is $m = \rho A_\text{s} \delta r$. Expressed as components in the direction of increasing r of the forces exerted on the volume element, the force at the inner face is pA_s, the force at the outer face is $-(p + \delta p)A_\text{s}$, and the centrifugal force is $m\omega^2 r = \rho A_\text{s} \omega^2 r \delta r$. From Newton's second law, the sum of these components is zero at equilibrium:

$$pA_{\text{s}} - (p+\delta p)A_{\text{s}} + \rho A_{\text{s}}\omega^2 r\delta r = 0 \qquad (9.8.10)$$

or $\delta p = \rho\omega^2 r\delta r$. In the limit as δr and δp are made infinitesimal, this becomes

$$\mathrm{d}p = \rho\omega^2 r\,\mathrm{d}r \qquad (9.8.11)$$

We will assume the density ρ is uniform throughout the solution. (In the centrifugal field, this assumption is strictly true only if the solution is incompressible and its density is independent of composition.) Then integration of Eq. 9.8.11 yields

$$p'' - p' = \int_{p'}^{p''} \mathrm{d}p = \rho\omega^2 \int_{r'}^{r''} r\,\mathrm{d}r = \frac{\rho\omega^2}{2}\left[(r'')^2 - (r')^2\right] \qquad (9.8.12)$$

where the superscripts $'$ and $''$ denote positions at two different values of r in the cell. The pressure is seen to increase with increasing distance from the axis of rotation.

Next we investigate the dependence of the solute concentration c_{B} on r in the equilibrium state of the binary solution. Consider a small sample of the solution of mass m. Assume the extent of this sample in the radial direction is small enough for the variation of the centrifugal force field to be negligible. The reversible work in the local frame needed to move this small sample an infinitesimal distance $\mathrm{d}r$ at constant z, T, and p, using an external force $-F^{\text{centr}}$ that opposes the centrifugal force, is

$$đw' = F^{\text{sur}}\,\mathrm{d}r = (-F^{\text{centr}})\,\mathrm{d}r = -m\omega^2 r\,\mathrm{d}r \qquad (9.8.13)$$

This work is a contribution to the change $\mathrm{d}U$ of the internal energy. The Gibbs energy of the small sample in the local frame is a function of the independent variables T, p, n_{A}, n_{B}, and r, and its total differential is

$$\begin{aligned}
\mathrm{d}G &= \mathrm{d}(U - TS + pV)\\
&= -S\,\mathrm{d}T + V\,\mathrm{d}p + \mu_{\text{A}}\,\mathrm{d}n_{\text{A}} + \mu_{\text{B}}\,\mathrm{d}n_{\text{B}} - m\omega^2 r\,\mathrm{d}r
\end{aligned} \qquad (9.8.14)$$

We use Eq. 9.8.14 to write the reciprocity relation

$$\left(\frac{\partial\mu_{\text{B}}}{\partial r}\right)_{T,p,n_{\text{A}},n_{\text{B}}} = -\omega^2 r\left(\frac{\partial m}{\partial n_{\text{B}}}\right)_{T,p,n_{\text{A}},r} \qquad (9.8.15)$$

Then, using $m = n_{\text{A}}M_{\text{A}} + n_{\text{B}}M_{\text{B}}$, we obtain

$$\left(\frac{\partial\mu_{\text{B}}}{\partial r}\right)_{T,p,n_{\text{A}},n_{\text{B}}} = -M_{\text{B}}\omega^2 r \qquad (9.8.16)$$

Thus at constant T, p, and composition, which are the conditions that allow the activity $a_{c,\text{B}}$ to remain constant, μ_{B} for the sample varies with r according to $\mathrm{d}\mu_{\text{B}} = -M_{\text{B}}\omega^2 r\,\mathrm{d}r$. We integrate from radial position r' to position r'' to obtain

$$\begin{aligned}
\mu_{\text{B}}(r'') - \mu_{\text{B}}(r') &= -M_{\text{B}}\omega^2 \int_{r'}^{r''} r\,\mathrm{d}r\\
&= -\tfrac{1}{2}M_{\text{B}}\omega^2\left[(r'')^2 - (r')^2\right]
\end{aligned} \qquad \substack{(9.8.17)\\ (a_{c,\text{B}}(r'')=a_{c,\text{B}}(r'))}$$

Let us take r' as a reference position, such as the end of the centrifuge cell farthest from the axis of rotation. We define the standard chemical potential $\mu_{c,\text{B}}^{\circ}$ as the solute chemical potential under standard state conditions on a concentration basis at this position. The solute chemical potential and activity at this position are related by

$$\mu_{\text{B}}(r') = \mu_{c,\text{B}}^{\circ} + RT\ln a_{c,\text{B}}(r') \qquad (9.8.18)$$

From Eqs. 9.8.17 and 9.8.18, we obtain the following general relation between μ_{B} and $a_{c,\text{B}}$ at an arbitrary radial position r'':

$$\mu_{\text{B}}(r'') = \mu_{c,\text{B}}^{\circ} + RT\ln a_{c,\text{B}}(r'') - \tfrac{1}{2}M_{\text{B}}\omega^2\left[(r'')^2 - (r')^2\right] \qquad (9.8.19)$$

We found earlier that when the solution is in an equilibrium state, μ_{B} is independent of r—that is, $\mu_{\text{B}}(r'')$ is equal to $\mu_{\text{B}}(r')$ for any value of r''. When we equate expressions given by Eq. 9.8.19 for $\mu_{\text{B}}(r'')$ and $\mu_{\text{B}}(r')$ and rearrange, we obtain the following relation between the activities at the two radial positions:

$$\ln \frac{a_{c,B}(r'')}{a_{c,B}(r')} = \frac{M_B \omega^2}{2RT} \left[(r'')^2 - (r')^2 \right]$$

<div align="right">(9.8.20)
(solution in centrifuge
cell at equilibrium)</div>

The solute activity is related to the concentration c_B by $a_{c,B} = \Gamma_{c,B} \gamma_{c,B} c_B / c^\circ$. We assume the solution is sufficiently dilute for the activity coefficient $\gamma_{c,B}$ to be approximated by 1. The pressure factor is given by $\Gamma_{c,B} \approx \exp\left[V_B^\infty (p - p^\circ)/RT\right]$ (Table 9.6). These relations give us another expression for the logarithm of the ratio of activities:

$$\ln \frac{a_{c,B}(r'')}{a_{c,B}(r')} = \frac{V_B^\infty (p'' - p')}{RT} + \ln \frac{c_B(r'')}{c_B(r')}$$

<div align="right">(9.8.21)</div>

We substitute for $p'' - p'$ from Eq. 9.8.12. It is also useful to make the substitution $V_B^\infty = M_B v_B^\infty$, where v_B^∞ is the partial specific volume of the solute at infinite dilution.

When we equate the two expressions for $\ln[a_{c,B}(r'')/a_{c,B}(r')]$, we obtain finally

$$\ln \frac{c_B(r'')}{c_B(r')} = \frac{M_B \left(1 - v_B^\infty \rho\right) \omega^2}{2RT} \left[(r'')^2 - (r')^2 \right]$$

<div align="right">(9.8.22)
(solution in centrifuge
cell at equilibrium)</div>

This equation shows that if the solution density ρ is less than the effective solute density $1/v_B^\infty$, so that $v_B^\infty \rho$ is less than 1, the solute concentration increases with increasing distance from the axis of rotation in the equilibrium state. If, however, ρ is greater than $1/v_B^\infty$, the concentration decreases with increasing r. The factor $\left(1 - v_B^\infty \rho\right)$ is like a buoyancy factor for the effect of the centrifugal field on the solute.

Equation 9.8.22 is needed for *sedimentation equilibrium*, a method of determining the molar mass of a macromolecule. A dilute solution of the macromolecule is placed in the cell of an analytical ultracentrifuge, and the angular velocity is selected to produce a measurable solute concentration gradient at equilibrium. The solute concentration is measured optically as a function of r. The equation predicts that a plot of $\ln(c_B/c^\circ)$ versus r^2 will be linear, with a slope equal to $M_B \left(1 - v_B^\infty \rho\right) \omega^2 / 2RT$. The partial specific volume v_B^∞ is found from measurements of solution density as a function of solute mass fraction (Sec. 9.2.5). By this means, the molar mass M_B of the macromolecule is evaluated.