Chapter 20
The Chemical Potential

20.1 Definition and Interpretation

Changes in the composition of the mixture, either by addition or removal of components or by reaction, change the properties of the mixture, in particular the Gibbs free energy. A straightforward extension of the Gibbs equation which accounts for the change of Gibbs free energy with varying composition is

$$dG = -SdT + Vdp + \sum_{\alpha=1}^{\nu} \bar{\mu}_\alpha dn_\alpha \ , \tag{20.1}$$

where the new quantity $\bar{\mu}_\alpha$ is the *chemical potential.* We have by definition,

$$\bar{\mu}_\gamma = \left(\frac{\partial G}{\partial n_\gamma}\right)_{T,p,n_\alpha(\alpha\neq\gamma)} \ . \tag{20.2}$$

The chemical potential is of fundamental importance in the thermodynamics of inert and reacting mixtures. To understand its physical meaning, we consider two mixtures of different composition and different pressures but equal temperatures T, which are divided by a semi-permeable membrane that only allows component γ to pass, as depicted in Fig. 20.1. Since pressure and temperature are controlled, we know that in equilibrium the Gibbs free energy of the system must assume a minimum,

$$G \longrightarrow \text{Minimum} \ . \tag{20.3}$$

The total Gibbs free energy of the system is the sum of the Gibbs free energies of the two parts I and II of the system, which depend only on the pressure, temperature and mole numbers within their portion of the system,

$$G = G^{\mathrm{I}}\left(T, p^{\mathrm{I}}, n_1^{\mathrm{I}}, \ldots, n_\gamma^{\mathrm{I}}, \ldots, n_{\nu_{\mathrm{I}}}^{\mathrm{I}}\right) + G^{\mathrm{II}}\left(T, p^{\mathrm{II}}, n_1^{\mathrm{II}}, \ldots, n_\gamma^{\mathrm{II}}, \ldots, n_{\nu_{\mathrm{II}}}^{\mathrm{II}}\right) \ . \tag{20.4}$$

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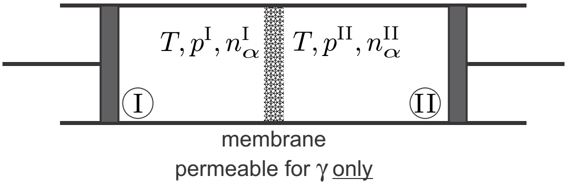

Fig. 20.1 System divided by semi-permeable membrane

Only the mole numbers n_γ^{I} and $n_\gamma^{\mathrm{II}} = n_\gamma - n_\gamma^{\mathrm{I}}$ can change due to migration through the semi-permeable membrane. All other mole numbers $(n_\alpha^{\mathrm{I}}, n_\alpha^{\mathrm{II}})$, the pressures $(p^{\mathrm{I}}, p^{\mathrm{II}})$ and the temperature T are fixed. Thus, the condition for equilibrium of the system, where G is at a minimum, is

$$\left(\frac{\partial G^{\mathrm{I}}}{\partial n_\gamma^{\mathrm{I}}}\right)_{T,p^{\mathrm{I}},n_\alpha^{\mathrm{I}}(\alpha\neq\gamma)} + \left(\frac{\partial G^{\mathrm{II}}}{\partial n_\gamma^{\mathrm{I}}}\right)_{T,p^{\mathrm{II}},n_\alpha^{\mathrm{II}}(\alpha\neq\gamma)} = 0 \tag{20.5}$$

or, since $n_\gamma^{\mathrm{I}} + n_\gamma^{\mathrm{II}} = n_\gamma = const.$ and thus $\frac{\partial}{\partial n_\gamma^{\mathrm{I}}} = -\frac{\partial}{\partial n_\gamma^{\mathrm{II}}}$,

$$\bar{\mu}_\gamma^{\mathrm{I}} = \left(\frac{\partial G^{\mathrm{I}}}{\partial n_\gamma^{\mathrm{I}}}\right)_{T,p^{\mathrm{I}},n_\alpha^{\mathrm{I}}(\alpha\neq\gamma)} = \left(\frac{\partial G^{\mathrm{II}}}{\partial n_\gamma^{\mathrm{II}}}\right)_{T,p^{\mathrm{II}},n_\alpha^{\mathrm{II}}(\alpha\neq\gamma)} = \bar{\mu}_\gamma^{\mathrm{II}} \ . \tag{20.6}$$

In short, in thermodynamic equilibrium, the chemical potentials of the substance γ that can pass through a semipermeable membrane are equal,

$$\bar{\mu}_\gamma\left(T, p^{\mathrm{I}}, n_\alpha^{\mathrm{I}}\right) = \bar{\mu}_\gamma\left(T, p^{\mathrm{II}}, n_\alpha^{\mathrm{II}}\right) \ . \tag{20.7}$$

Just as the continuity of temperature at diathermic walls allows us to measure temperature, the continuity of the chemical potential at semi-permeable walls allows us its measurement, at least in principle. And just as temperature differences lead to heat flow and allow for power generation, differences in chemical potential cause particle flow and allow for power generation, as will be discussed in Section 20.7.

Nevertheless, the chemical potential is a rather abstract quantity, and we need to study it further, and relate it to quantities we are more familiar with.

20.2 Properties of the Chemical Potential

The Gibbs free energy $G(T, p, n_\beta)$ is an extensive quantity, which implies that it is a homogeneous function of mole number,

$$zG(T, p, n_\beta) = G(T, p, zn_\beta) \ . \tag{20.8}$$

We take the derivative of the above with respect to z, to obtain

$$\begin{aligned} G\left(T,p,n_{\beta}\right) &= \sum_{\alpha=1}^{\nu} \frac{\partial G\left(T,p,zn_{\beta}\right)}{\partial\left(zn_{\alpha}\right)} \frac{d\left(zn_{\alpha}\right)}{dz} \\ &= \sum_{\alpha=1}^{\nu} \frac{\partial G\left(T,p,zn_{\beta}\right)}{\partial\left(zn_{\alpha}\right)} n_{\alpha} = \sum_{\alpha=1}^{\nu} \bar{\mu}_{\alpha}\left(T,p,zn_{\beta}\right) n_{\alpha} \ . \end{aligned} \tag{20.9}$$

This must hold for all z. Since the left hand side is independent of z, the right hand side should not depend on z as well. This is so, when the chemical potential does not depend on all mole numbers n_{β}, but only on quotients like the mole ratio X_{β}, which is independent of z, since $X_{\beta}\left(n_{\gamma}\right) = \frac{n_{\beta}}{n}$, so that $X_{\beta}\left(zn_{\gamma}\right) = X_{\beta}\left(n_{\gamma}\right)$. Thus we have

$$\bar{\mu}_{\alpha} = \bar{\mu}_{\alpha}\left(T,p,X_{\beta}\right) \ . \tag{20.10}$$

With this we obtain from (20.9)

$$G\left(T,p,n_{\beta}\right) = \sum_{\alpha=1}^{\nu} n_{\alpha}\bar{\mu}_{\alpha}\left(T,p,X_{\beta}\right) \ . \tag{20.11}$$

According to (20.11), in a mixture the total Gibbs free energy is the sum of the component mole numbers times their chemical potentials, $G = \sum n_{\alpha}\bar{\mu}_{\alpha}$. Since

$$G = H - TS = \sum_{\alpha=1}^{\nu} n_{\alpha}\bar{h}_{\alpha} - T\sum_{\alpha=1}^{\nu} n_{\alpha}\bar{s}_{\alpha} = \sum_{\alpha=1}^{\nu} n_{\alpha}\left(\bar{h}_{\alpha} - T\bar{s}_{\alpha}\right) \ , \tag{20.12}$$

this implies that the chemical potential is the specific Gibbs free energy of the component in the mixture, in the sense that

$$\bar{\mu}_{\alpha}\left(T,p,X_{\beta}\right) = \bar{h}_{\alpha}\left(T,p,X_{\beta}\right) - T\bar{s}_{\alpha}\left(T,p,X_{\beta}\right) \ . \tag{20.13}$$

Here, $\bar{h}_{\alpha}\left(T,p,X_{\beta}\right)$ and $\bar{s}_{\alpha}\left(T,p,X_{\beta}\right)$ are the specific enthalpy and entropy of component α in the mixture at temperature T, pressure p, and composition X_{β}.

The molar Gibbs free energy of the mixture is defined as

$$\bar{g} = \frac{G}{n} = \sum_{\alpha=1}^{\nu} X_{\alpha}\bar{\mu}_{\alpha}\left(T,p,X_{\beta}\right) \ . \tag{20.14}$$

For a single substance the chemical potential is equal to the molar Gibbs free energy,

$$G = n\bar{g} = n\bar{\mu} \quad \text{so that} \quad \bar{\mu}\left(T,p\right) = \bar{g}\left(T,p\right) \ . \tag{20.15}$$

For this reason, one sometimes finds the specific Gibbs free energy denoted as the chemical potential. For the description of the component, it is useful to distinguish between the Gibbs free energy $\bar{g}_\alpha(T,p)$ that describes the component α alone at (T,p) and the chemical potential $\bar{\mu}_\alpha(T,p,X_\beta)$ that describes the component α in a mixture at (T,p) with mole fractions X_β, $\beta = 1,\ldots,\nu$.

Since the order of derivatives can be exchanged, we have the symmetry property

$$\frac{\partial \bar{\mu}_\beta}{\partial n_\gamma} = \frac{\partial^2 G}{\partial n_\gamma \partial n_\beta} = \frac{\partial^2 G}{\partial n_\beta \partial n_\gamma} = \frac{\partial \bar{\mu}_\gamma}{\partial n_\beta}\ . \tag{20.16}$$

20.3 Gibbs and Gibbs-Duhem Equations

We revisit the Gibbs equation for the mixture (20.1),

$$dG = -SdT + Vdp + \sum_{\alpha=1}^{\nu} \bar{\mu}_\alpha dn_\alpha\ . \tag{20.17}$$

The Gibbs equation for molar quantities of the mixture follows by setting $G = n\bar{g}$, $S = n\bar{s}$, $V = n\bar{v}$ and $n_\alpha = nX_\alpha$ as

$$d\bar{g} = -\bar{s}dT + \bar{v}dp + \sum_{\alpha=1}^{\nu} \bar{\mu}_\alpha dX_\alpha\ . \tag{20.18}$$

Alternative forms of the Gibbs equation can be obtained through Legendre transforms, which yield, e.g.,

$$Td\bar{s} = d\bar{u} + pd\bar{v} - \sum_{\alpha=1}^{\nu} \bar{\mu}_\alpha dX_\alpha\ . \tag{20.19}$$

As discussed in Sec. 16.2, the Gibbs equation leads to Maxwell relations, such as

$$\left(\frac{\partial \mu_\alpha}{\partial T}\right)_{p,X_\beta} = -\left(\frac{\partial \bar{s}}{\partial X_\alpha}\right)_{T,p,X_\beta} \quad , \quad \left(\frac{\partial \mu_\alpha}{\partial p}\right)_{T,X_\beta} = \left(\frac{\partial \bar{v}}{\partial X_\alpha}\right)_{T,p,X_\beta}\ . \tag{20.20}$$

With another Legendre transform (20.17) can be rewritten as

$$dG = -SdT + Vdp + \sum_{\alpha=1}^{\nu} d\left(\bar{\mu}_\alpha n_\alpha\right) - \sum_{\alpha=1}^{\nu} n_\alpha d\bar{\mu}_\alpha\ , \tag{20.21}$$

which, together with (20.11), yields the Gibbs-Duhem relation

$$0 = -SdT + Vdp - \sum_{\alpha=1}^{\nu} n_\alpha d\bar{\mu}_\alpha \ . \tag{20.22}$$

Taking the derivative of the Gibbs-Duhem relation (20.22) with respect to a mole number n_γ yields, with the symmetry property (20.16),

$$\sum_{\alpha=1}^{\nu} n_\alpha \left(\frac{\partial \bar{\mu}_\alpha}{\partial n_\gamma}\right)_{T,p,n_{\beta(\beta\neq\gamma)}} = \sum_{\alpha=1}^{\nu} n_\alpha \left(\frac{\partial \bar{\mu}_\gamma}{\partial n_\alpha}\right)_{T,p,n_{\beta(\beta\neq\gamma)}} = 0 \ . \tag{20.23}$$

20.4 Mass Based Chemical Potential

It is an easy exercise to translate the above mole based relations into mass based relations, which read

$$dG = -SdT + Vdp + \sum_{\alpha=1}^{\nu} \mu_\alpha dm_\alpha \ , \tag{20.24}$$

$$dg = -sdT + vdp + \sum_{\alpha=1}^{\nu} \mu_\alpha dc_\alpha \ , \tag{20.25}$$

$$\mu_\alpha = \left(\frac{\partial G}{\partial m_\gamma}\right)_{T,p,m_\alpha(\alpha\neq\gamma)} \ , \tag{20.26}$$

$$\mu_\alpha = \mu_\alpha\left(T,p,c_\beta\right) \ , \tag{20.27}$$

$$G\left(T,p,m_\beta\right) = \sum_{\alpha=1}^{\nu} m_\alpha \mu_\alpha\left(T,p,c_\beta\right) \ , \tag{20.28}$$

$$\mu_\alpha\left(T,p,c_\beta\right) = h_\alpha\left(T,p,c_\beta\right) - Ts_\alpha\left(T,p,c_\beta\right) \ , \tag{20.29}$$

$$\mu\left(T,p\right) = g\left(T,p\right) \ , \tag{20.30}$$

$$\frac{\partial \mu_\beta}{\partial m_\gamma} = \frac{\partial \mu_\gamma}{\partial m_\beta} \ , \tag{20.31}$$

$$0 = -SdT + Vdp - \sum_{\alpha=1}^{\nu} m_\alpha d\mu_\alpha \ , \tag{20.32}$$

$$\sum_{\alpha=1}^{\nu} m_\alpha \left(\frac{\partial \mu_\alpha}{\partial m_\gamma}\right)_{T,p,m_{\beta(\beta\neq\gamma)}} = \sum_{\alpha=1}^{\nu} m_\alpha \left(\frac{\partial \mu_\gamma}{\partial m_\alpha}\right)_{T,p,m_{\beta(\beta\neq\gamma)}} = 0 \ . \tag{20.33}$$

The verification of the above is left to the reader.

20.5 The Chemical Potential for an Ideal Mixture

The Gibbs free energy of an ideal mixture at (T, p) is given by

$$G = \sum_{\alpha=1}^{\nu} n_\alpha \bar{\mu}_\alpha = \sum_{\alpha=1}^{\nu} n_\alpha \bar{g}_\alpha + H_{\text{mix}} - T S_{\text{mix}} \ , \tag{20.34}$$

where $\sum_\alpha n_\alpha \bar{g}_\alpha$ is the Gibbs free energy of the unmixed state, and $H_{\text{mix}} - TS_{\text{mix}}$ is the Gibbs free energy of mixing. For the ideal mixture $H_{\text{mix}} = 0$, and S_{mix} is given by (18.26) so that

$$G = \sum_{\alpha=1}^{\nu} n_\alpha \bar{\mu}_\alpha = \sum_{\alpha=1}^{\nu} n_\alpha \bar{g}_\alpha + \bar{R} T \sum_{\alpha=1}^{\nu} n_\alpha \ln X_\alpha \ . \tag{20.35}$$

Thus the chemical potential of the ideal mixture is the sum of the Gibbs free energy of the component alone at mixing conditions (T, p) plus a contribution from the entropy of mixing,

$$\bar{\mu}_\alpha \left(T, p, X_\beta\right) = \bar{g}_\alpha \left(T, p\right) + \bar{R} T \ln X_\alpha \ . \tag{20.36}$$

20.6 The Chemical Potential for an Ideal Gas Mixture

Using that $g = h - Ts$ and the property relations for the ideal gas, the chemical potential of an ideal gas is

$$\bar{\mu}_\alpha \left(T, p, X_\beta\right) = \bar{h}_\alpha \left(T\right) - T \bar{s}_\alpha^0 \left(T\right) + \bar{R} T \ln \frac{X_\alpha p}{p_0} \ . \tag{20.37}$$

As an example we study two ideal gas mixtures at $\left(T, p^{\text{I}}\right)$ and $\left(T, p^{\text{II}}\right)$, separated by a semi-permeable membrane that only allows component ν to pass. The equilibrium condition (20.7) is

$$\bar{\mu}_\nu \left(T, p^{\text{I}}, X_\beta^{I}\right) = \bar{\mu}_\nu \left(T, p^{\text{II}}, X_\beta^{\text{II}}\right) \ , \tag{20.38}$$

and evaluation with (20.37) gives

$$X_\nu^{\text{I}} p^{\text{I}} = X_\nu^{\text{II}} p^{\text{II}} \ . \tag{20.39}$$

Thus, we find the intuitive result that for an ideal gas the partial pressure $p_\nu = X_\nu p$ is continuous at the ideal semipermeable membrane. This means, that the component that can pass the membrane behaves as if the membrane is not present, it is homogeneously distributed over the entire accessible volume.

20.7 The Chemical Potential as Driving Force for Mass Transfer

We consider the set-up shown in Fig. 20.2: Two reservoirs I and II contain mixtures of different temperature T, pressure p, and composition X_α, which remain constant at all times. Through semipermeable membranes the two reservoirs are connected to a heat and mass conducting duct. Due to the non-equilibrium between the two reservoirs we expect flows of mass and heat. The duct might contain devices to extract work from these flows.

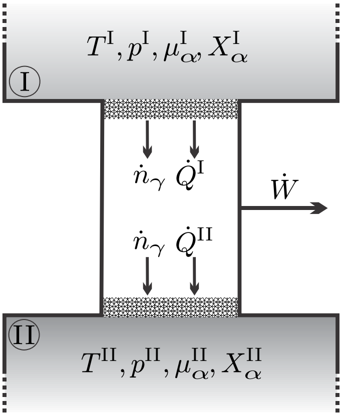

Fig. 20.2 Chemical potential difference as driving force

The membranes let only component γ pass and we consider only steady state processes. Since only component γ passes through membranes and duct, the first and second law for the duct read

$$\dot{n}_\gamma\left(\bar{h}_\gamma^{\mathrm{II}} - \bar{h}_\gamma^{\mathrm{I}}\right) = \dot{Q}^{\mathrm{I}} + \dot{Q}^{\mathrm{II}} - \dot{W} \quad , \quad \dot{n}_\gamma\left(\bar{s}_\gamma^{\mathrm{II}} - \bar{s}_\gamma^{\mathrm{I}}\right) = \frac{\dot{Q}^{\mathrm{II}}}{T^{\mathrm{II}}} + \frac{\dot{Q}^{\mathrm{I}}}{T^{\mathrm{I}}} + \dot{S}_{gen} \ . \tag{20.40}$$

Elimination of the heat rejected to reservoir II gives, with $\bar{s}_\gamma = \frac{\bar{h}_\gamma - \bar{\mu}_\gamma}{T}$,

$$\dot{W} + T^{\mathrm{II}}\dot{S}_{gen} = \dot{n}_\gamma T^{\mathrm{II}}\left[\frac{\bar{\mu}_\gamma^{\mathrm{I}}}{T^{\mathrm{I}}} - \frac{\bar{\mu}_\gamma^{\mathrm{II}}}{T^{\mathrm{II}}}\right] + \left(\dot{n}_\gamma \bar{h}_\gamma^{\mathrm{I}} + \dot{Q}^{\mathrm{I}}\right)\left[1 - \frac{T^{\mathrm{II}}}{T^{\mathrm{I}}}\right] \ . \tag{20.41}$$

The right hand side of this equation vanishes in the case of thermal and chemical equilibrium, where $T^{\mathrm{I}} = T^{\mathrm{II}}$ and $\mu_\gamma^{\mathrm{I}} = \mu_\gamma^{\mathrm{II}}$.

Power can be generated from the differences in temperature and chemical potential. We have studied heat engines, which are driven by temperature differences, in great detail in previous chapters. The generation of power from differences in the chemical potential, known as osmotic power generation, will be discussed further below. The maximum possible power is generated when transfer through the duct occurs fully reversibly, so that $\dot{S}_{gen} = 0$.

When the duct is fully irreversible, so that no power is generated, $\dot{W} = 0$, the amount of entropy produced (which must be non-negative) is

$$\dot{S}_{gen} = \dot{n}_\gamma \left[\frac{\bar{\mu}_\gamma^{\mathrm{I}}}{T^{\mathrm{I}}} - \frac{\bar{\mu}_\gamma^{\mathrm{II}}}{T^{\mathrm{II}}}\right] + \left(\dot{n}_\gamma \bar{h}_\gamma^{\mathrm{I}} + \dot{Q}^{\mathrm{I}}\right) \left[\frac{1}{T^{\mathrm{II}}} - \frac{1}{T^{\mathrm{I}}}\right] \geq 0 \,. \tag{20.42}$$

As before, in Sec. 4.10, we interpret the entropy generation in terms of thermodynamic forces and fluxes. The forces are the differences in reduced chemical potential, $\left[\frac{\bar{\mu}_\gamma^{\mathrm{I}}}{T^{\mathrm{I}}} - \frac{\bar{\mu}_\gamma^{\mathrm{II}}}{T^{\mathrm{II}}}\right]$, and inverse temperature, $\left[\frac{1}{T^{\mathrm{II}}} - \frac{1}{T^{\mathrm{I}}}\right]$, between the reservoirs. The related fluxes are the matter flow $\dot{n}_\gamma$ and the total energy flow $\left(\dot{n}_\gamma \bar{h}_\gamma^{\mathrm{I}} + \dot{Q}^{\mathrm{I}}\right)$. Previously, when we discussed Newton's law of cooling, we had only one flux-force pair, and set the flux proportional to the force. For the present setting, we have two such pairs, which offers a richer set of transport laws. Indeed, we allow for *both* forces to affect *both* fluxes, and write fluxes and forces as vectors, with a matrix of coefficients α_{ij},

$$\begin{bmatrix} \dot{n}_\gamma \\ \\ \dot{n}_\gamma \bar{h}_\gamma^{\mathrm{I}} + \dot{Q}^{\mathrm{I}} \end{bmatrix} = A \begin{bmatrix} \alpha_{11} & \alpha_{12} \\ \\ \alpha_{21} & \alpha_{22} \end{bmatrix} \cdot \begin{bmatrix} \frac{\bar{\mu}_\gamma^{\mathrm{I}}}{T^{\mathrm{I}}} - \frac{\bar{\mu}_\gamma^{\mathrm{II}}}{T^{\mathrm{II}}} \\ \\ \frac{1}{T^{\mathrm{II}}} - \frac{1}{T^{\mathrm{I}}} \end{bmatrix} \,. \tag{20.43}$$

As always, we made the transfer surface A explicit. To ensure positive entropy generation, the matrix of transport coefficients α_{ij} must be positive definite, which is the case for $\alpha_{11} > 0$ and $\alpha_{11}\alpha_{22} - \alpha_{12}\alpha_{21} > 0$.

We note that transfer of matter does not only occur due to differences in pressure (typical flow), and composition (diffusion), but also in response to a temperature gradient (thermodiffusion, or Soret effect, Charles Soret 1854-1904)). Heat transfer does not only occur due to a temperature difference, but also due to differences in pressure or composition (Dufour effect, Louis Dufour 1832-1892).

A deep discussion of laws of this type reveals the Onsager reciprocity relations (Lars Onsager, 1903-1976), which for this case state that the matrix must be symmetric, $\alpha_{21} = \alpha_{21}$. Careful experiments show that the so-called cross effects, which are described by the off-diagonal terms in the matrix, are less important than the direct effects, which are described by the diagonal terms. In engineering applications the cross effects are often ignored.[1]

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[1] The arguments we use here are typical in the field of Non-equilibrium Thermodynamics. A thorough yet accessible introduction into this topic is presented in: S. Kjelstrup, D. Bedeaux, E. Johannessen, J. Gross: *Non-equilibrium Thermodynamics for Engineers*, World Scientific, Singapore 2010.

When the flow $\dot{n}_\gamma$ goes from I to II as shown, the reduced chemical potential $\frac{\bar{\mu}_\gamma^{\mathrm{I}}}{T^{\mathrm{I}}}$ must be larger than $\frac{\bar{\mu}_\gamma^{\mathrm{II}}}{T^{\mathrm{II}}}$. In other words, a difference in chemical potential causes a flow against the gradient of the (reduced) chemical potential.

When we ignore temperature differences ($T^{\mathrm{I}} = T^{\mathrm{II}} = T$), we can expect a linear law of the form

$$\dot{n}_\nu = \kappa A \left[\bar{\mu}_\gamma^{\mathrm{I}} - \bar{\mu}_\gamma^{\mathrm{II}}\right] \ , \tag{20.44}$$

where $\kappa = \alpha_{11}/T$ is a positive constitutive coefficient, and A is the cross section of the duct.

In the special case when both mixtures are ideal, and have the same pressures and temperatures, we have $\bar{\mu}_\gamma^{\mathrm{I}} - \bar{\mu}_\gamma^{\mathrm{II}} = \bar{R}T \ln \frac{X_\gamma^{\mathrm{I}}}{X_\gamma^{\mathrm{II}}}$: there will be a particle flux unless both mole fractions are equilibrated.

In short, the desire to equilibrate the chemical potential leads to a flux of that component that can pass the duct. The flux direction is against the gradient, which reduces the gradient. According to Eq. (20.41), this flux can be used to produce power $\dot{W} > 0$. Inversion of the flux, that is forcing flow in the direction of the gradient, requires power input, $\dot{W} < 0$. This is fully equivalent to what we have seen on temperature differences: Heat will flow from hot to cold—against the gradient—by itself, and this heat flux can be used to produce power in a heat engine. Transferring heat from cold to hot—in the direction of the gradient—requires work input, i.e., a heat pump.

Problems

20.1. Symmetry Property for Ideal Mixture

For an ideal mixture, prove the symmetry property (20.16), as well as (20.23).

20.2. Chemical Potential for Ideal Mixture

Determine the chemical potential of an ideal mixture (20.36) by taking the derivative of (20.35), $\bar{\mu}_\alpha = \left(\frac{\partial G}{\partial n_\alpha}\right)_{T,p,n_\gamma}$.

20.3. Mass Based Chemical Potential

Derive the equations for the mass based chemical potential in Sec. 20.4.

20.4. Mass Based Chemical Potential for Ideal Mixture

Rewrite the Gibbs free energy of an ideal mixture (20.35) in terms of mass based quantities, $G\left(T, p, m_\beta\right)$ and determine the mass based chemical potential from the derivative, $\mu_\alpha = \left(\frac{\partial G}{\partial m_\alpha}\right)_{T,p,m_\gamma}$. Show that $\bar{\mu}_\alpha = M_\alpha \mu_\alpha$.

20.5. Gas Mixture

A semipermeable membrane which allows only hydrogen to pass divides two containers. In thermodynamic equilibrium container A holds 800 g of nitrogen and 150 g of hydrogen, while container B holds 1800 g of carbon dioxide and 100 g of hydrogen. Container A is kept at a pressure of 20 bar and the temperature of both containers is 300 K.

1. Determine the pressure in container B.
2. Determine the minimum work to separate the hydrogen out of container A.

20.6. Gas Mixture

A semipermeable membrane which allows only hydrogen to pass divides two containers which are kept at 300 K. Initially, container A holds 1000 g of CO_2 at 10 bar, and container B holds 300 g of O_2 at 20 bar. Now 400 g of H_2 are added to the system, such that the pressures of A and B do not change.

1. Determine the amounts of H_2 in containers A and B.
2. Determine the minimum work to separate the H_2 out of container A.

20.7. Gas Mixture

A semipermeable membrane which allows only N_2 to pass divides two containers which are kept at 350 K. Initially, container A holds 2 kg of CO_2 at 10 bar, and container B holds 3 kg of Xe at 20 bar. Now an unknown amount of nitrogen is added to the system, such that the pressures of A and B do not change. After thermodynamic equilibrium is established, it is observed that the volume of container A has increased by 25%.

1. Determine the amount of N_2 added to container A.
2. Determine the amount of N_2 added to container B.
3. Determine the minimum work to separate the nitrogen out of container A.

20.8. Gas Separation

A binary mixture of ideal gases (α, β) is to be partly separated. The mixture is at temperature $T = 300\,\mathrm{K}$ and the initial mole fraction is X_α^I. The goal is to separate half of the initial amount of α from the rest.

1. Determine the mole fraction of α in the mixture remaining after separation.
2. Show that the minimum work for separation is the difference in the entropy of mixing of the final and initial mixtures, times the temperature of the mixture.
3. Determine the minimum work for the required separation, per mole of separated component α.
4. Suppose a semipermeable membrane exists that allows only α to pass. Determine the pressure to which the mixture has to be compressed in order to achieve the desired separation; assume the separated gas is at pressure p_0.
5. Specify the results for minimum separation work and pressure for $X_\alpha^I = 0.5, 0.1, 0.01, 0.001, 0.0001$ and discuss the results. Would you think membrane separation makes sense? What would be the alternatives?

20.9. Ideal Gas in Gravitational Field

Show that in a mixture of ideal gases at temperature T_0 in the gravitational field ($\gamma = 9.81\,\frac{\mathrm{m}}{\mathrm{s}^2}$) the individual components obey the barometric formula. Hint: Minimize free energy to show first that $\bar{\mu}_\beta - \bar{R}T_0 + M_\beta \gamma z = const.$, and then evaluate the chemical potential for ideal gases.

20.10. Binary Mixture in Gravitational Field

An ideal liquid mixture of incompressible components $\alpha = 1, 2$ is enclosed in a piston cylinder system in the gravitational field. The pressure at the piston is p, and the system is kept at constant temperature T. The total mole numbers of the components are n_α, and their local mole densities are denoted as $\nu_\alpha(z)$ with $n_\alpha = \int_0^H \nu_\alpha(z)\, A dz$, where A is the constant cross section of the cylinder, z is the height coordinate, and H is actual height. To simplify the computation, assume that the total mole density is constant, $\nu_1(z) + \nu_2(z) = \nu_0$. By minimizing $G + E_{pot}$ (see Chapter 17) under constraints of given mole numbers n_α, find an equation for the mole fraction as function of height, $X_1(z) = \frac{\nu_1(z)}{\nu_0}$. Show that the mole fraction depends on the difference between molar masses M_α. Simplify for the case of a dilute solution, where $X_1 \ll 1$.

20.11. Gibbs Equation

Show that the Gibbs equation (20.25) leads to the alternative forms

$$Tds = du + pdv - \sum_\alpha \mu_\alpha dc_\alpha \quad , \quad df = -sdT - pdv + \sum_\alpha \mu_\alpha dc_\alpha \ .$$

20.12. Equilibrium in a Mixture

Consider a mixture in equilibrium under controlled volume, energy and partial masses. Maximize entropy

$$S = \int \rho s dV \ .$$

under the constraints

$$U = \int \rho u dV \quad , \quad m_\alpha = \int \rho c_\alpha dV \ ,$$

and show that in equilibrium pressure p, temperature T and chemical potential μ_α of all components are homogeneous. Use the Gibbs equation in the form

$$Tds = du + pdv - \sum_\alpha \mu_\alpha dc_\alpha \ .$$

Remark: s, u, v, μ_α are specific quantities (per unit mass of mixture); dm is the mass element of mixture. Use Lagrange multipliers.