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Membrane Thermodynamics for Osmotic Phenomena

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Abstract

In this chapter, we briefly review the thermodynamic ensembles and associated energy functions using the seven thermodynamic variables. The energy E , the entropy S , and the system volume V are used to derive the temperature T and pressure P . The chemical potential μ is derived as the change of the system energy with respect to the number of matters N in the isobaric-isothermal environment. A dilute solution is defined as a homogeneous mixture of solvent and inert solutes, where the total number and volume of solutes are much smaller than those of the solvent. Gibbs free energy of the dilute solution is used to rigorously derive the osmotic pressure by equilibrating chemical potentials of solutes and solvent. Nonequilibrium of the filtration systems is reviewed by introducing the irreversible thermodynamic model with Onsager's reciprocal theorem. Direct applications of the irreversible thermodynamic model are currently limited due to the absence of the exact nonequilibrium statistical mechanics. We hope this chapter, containing a review of statistical mechanics, related to membrane separations and osmosis phenomena, helps researchers and especially graduate students, who seek an in-depth understanding of membrane separation from the theoretical statistical physics as applied to chemical and environmental engineering.

Keywords: membrane thermodynamics, statistical mechanics, thermodynamic ensemble, Gibbs energy function, chemical potential, weak solution, osmotic pressure, Fick's law, solution-diffusion model, thermodynamic irreversible model

1. Introduction

A membrane is a selective barrier between two phases, i.e., a thin layer of material that separates solute and solvent materials when a driving force is applied across it. On membrane surfaces, flows of different thermodynamic phases are introduced and maintained quasi-steady with respect to time. These separation processes require driving forces mainly for

mass transfer as gradients of physical quantities associated with the thermodynamic, flowing phases.

Separation implies collecting masses of the same particles/molecules in specific spatial locations, which is strongly correlated to diffusion phenomena. Nature tends to move from a higher energy to a lower energy state, or equivalently highly ordered to randomly disordered phases. The diffusion of solutes in a free (solvent) medium is a spontaneous tendency, which must be well understood to analyze the separation phenomena. On the other hand, if the solutes are spatially confined by permeable interfaces, through which only solvent molecules can pass, the solvents try to move from their high- to low-concentration sides. This phenomena is called *osmosis*, which is equivalent to the solvent moving from low- to high-concentration regions of solutes. Note that in the solute diffusion and the solvent osmosis processes, mass transfer phenomena are from high- to low-concentration regions of the transferring masses. In this light, diffusion and osmosis can be treated equivalently as energy-minimizing and entropy-increasing phenomena of solutes and solvents, respectively.

Most pressure-driven membrane separations aim to produce clean water (solvent) from concentrated solutions. These include ultrafiltration (UF) and microfiltration (MF) for particulate removal and reverse osmosis (RO) and nanofiltration (NF) for ion removal. UF uses a finely porous membrane, which is usually antisymmetric, having a mean pore diameter between 1 and 100 nm. UF aims to separate water and microsolute from macromolecules and colloids [1–3]. MF uses porous membranes to separate suspended particles with diameters between 0.1 and 10 μm [1, 3, 4]. MF's filtration capacity is therefore between UF and conventional filtration methods. Based on the particle size, dominant diffusion mechanisms of these particulate matters include Brownian diffusion [5–9] and shear-induced diffusion [10–12]. Ballistic motion of non-Brownian particles (usually bigger than 10 μm) in MF can be treated as dynamics of inelastic granules. RO is a desalting process for water production using nonporous membranes that are permeable to water but essentially impermeable to salt. A pressurized feed stream containing dissolved salts contacts the feed-side of the RO membrane, and salt-depleted water is withdrawn as a low-pressure permeate stream [13–16]. NF membranes have lower rejection ratio, i.e., 20–80% of sodium chloride, than that of RO, typically greater than 98–99%. NF resides therefore between UF and RO in terms of salt rejection capability. High hydraulic pressure is an essential component for RO and NF to overcome the osmotic pressure of seawater and brackish water, respectively [17–21].

The concentration (equivalently, osmotic pressure) gradient can be used, however, as a driving force for forward osmosis (FO) and pressure-retarded osmosis (PRO) processes. FO extracts a solvent from the low- to high-concentration sides of the solutes in order to equilibrate the concentrations [22–25]. PRO utilizes the extra gains of hydraulic pressure due to the amount of the transferred solvent for power generation [26–29]. Both pressure-driven and osmosis-driven processes aim to achieve a high flux, i.e., a large amount of water produced per unit time per unit membrane surface area. In order to achieve a steady high flux, increases and decreases in the osmotic pressure gradient need to be prevented in the pressure- and osmosis-driven membrane processes, respectively. Therefore, maintaining a stable osmotic pressure is a primary issue in both types of processes.

The driving forces for membrane separations described above include gradients of the hydraulic pressure, solute concentration, solution temperature, and external electromagnetic field. In statistical mechanics, there are seven primary variables used to explain macroscopic thermodynamic phenomena. An ensemble is made using a set of three selected variables, and a specific energy function of the ensemble is described in terms of the three independent variables. As the membrane separations are coupled phenomena of momentum, mass, and heat transfer, a holistic understanding of statistical mechanics can significantly enhance design, analysis, and optimization of the membrane processes. In this chapter, we explain ensembles and energy functions in statistical mechanics, represent the osmotic pressure using Gibbs energy function of a weak (dilute) solution, and apply statistical laws to explain the separation phenomena using a solution-diffusion model [30].

2. Thermodynamics to statistical mechanics

Statistical mechanics is the microscopic version of thermodynamics [31]. Macroscopic quantities, dealt within thermodynamics, can be fundamentally obtained at the microscopic level in statistical mechanics. There are seven variables in thermodynamics, which are energy E , entropy S , temperature T , pressure P , volume V , number of molecules N , and chemical potential μ . An ensemble is defined as a set, in which three independent variables are used to define a specific form of an energy and the other four variables are represented as functions of the three master variables. For example, the elementary microcanonical ensemble has P , V , S , and μ , represented as functions of three master variables of N , V , and E .

2.1. Primary macroscopic quantities

2.1.1. Temperature

Consider two boxes in contact containing a certain number of particles in equilibrium, forming a closed system. Then, entropy S of the total system has its maximum value for a given system energy, E , i.e.,

$$S = S_{\max} \quad (1)$$

Since the energy is an additive scalar, the total energy of the entire system is the sum of the energies:

$$E = E_1 + E_2 \quad (2)$$

The total entropy can be similarly expressed, knowing that the entropy is a function of the energy:

$$S_{\max} = S_1(E_1) + S_2(E_2) \quad (3)$$

Since the entropy is already maximized in the equilibrium state, it is independent of the energy variation, i.e.,

$$\frac{dS}{dE_1} = \frac{dS_1}{dE_1} + \frac{dS_2}{dE_2} \frac{dE_2}{dE_1} = \frac{dS_1}{dE_1} - \frac{dS_2}{dE_2} = 0 \quad (4)$$

hence, we obtain

$$\frac{dS_1}{dE_1} = \frac{dS_2}{dE_2} \quad (5)$$

The derivative of the entropy S with respect to its energy E is used to define temperature as follows:

$$\frac{dS}{dE} \equiv \frac{1}{T} \quad \left(\rightarrow \frac{1}{k_B T} \right) \quad (6)$$

In the original definition, the magnitude of the temperature is too high so Boltzmann's constant k_B is introduced as shown in the parenthesis of Eq. (6). Temperature T is now represented in terms of the Kelvin unit. Substitution of Eq. (6) into Eq. (5) for each box provides

$$T_1 = T_2 \quad (7)$$

as a condition for the equilibrium. It is worth noting that the internal energy E and entropy S are the basic thermodynamic quantities, and the temperature is a derived variable proportional to the variation of E with respect to S (specifically, in the microcanonical ensemble).

2.1.2. Pressure

In fluid mechanics, pressure is often defined as the ratio of applied force per unit surface area of an object [32]:

$$P = \frac{\langle F_n \rangle}{\text{Area}} \quad (8)$$

where $\langle F_n \rangle$ is the mean normal component of the force vector \vec{F} applied to the object's surface area. A conservative force can be represented as a negative gradient of the total energy $E = K + U$, as a sum of kinetic energy K and potential energy U . Suppose the applied force causes an infinitesimal change in the volume of the body from V to $V + \delta V$ as shown in **Figure 1**. Then, the compressed volume is equal to the surface area multiplied by the thickness variation, i.e., $\delta V = A \delta s$, which is in general, $A = \vec{n} \cdot \nabla V$. Using the chain rule, one can represent the normal component of the applied force as a product of the energy density and the total surface area, which is

$$\vec{F} = -\nabla E = -\left(\frac{\partial E}{\partial V} \right)_s \nabla V \quad (9)$$

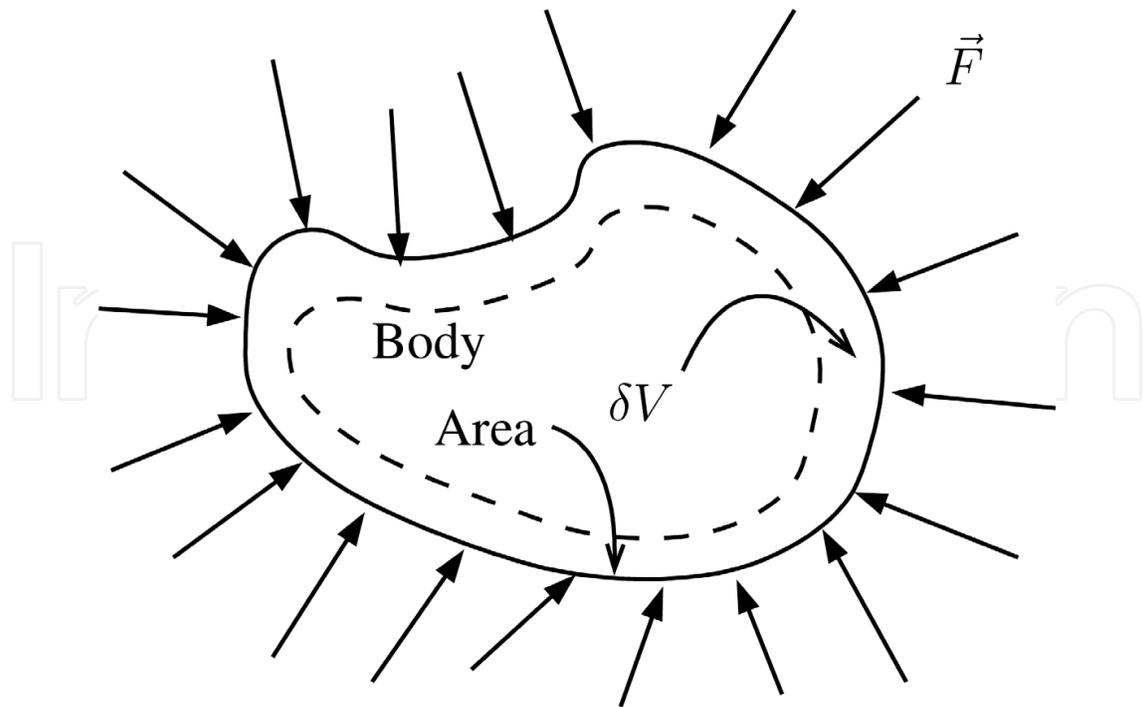


Figure 1. External forces applied to the surface of a body.

where, without losing generality, $(\partial E/\partial V)_S$ can be interpreted as the isentropic (i.e., of constant entropy) energy density inside the body volume V . One can operate the dot product by the normal vector \vec{n} on the left side of Eq. (9) to have

$$\vec{F} \cdot \vec{n} = F_n = -\left(\frac{\partial E}{\partial V}\right)_S A \quad (10)$$

and dividing both sides of Eq. (10) by the area A gives the conceptual definition of the pressure:

$$P = -\left(\frac{\partial E}{\partial V}\right)_S \quad (11)$$

Here, pressure definition can be extended from the normal force per unit area to the energy density in magnitude. Because energy E is a scalar quantity, the direction of the force vector does not need to be considered in the pressure calculation.

2.2. Ensembles and energy functions

2.2.1. Internal energy in microcanonical ensemble

In the previous section, we used three thermodynamic variables of energy E , entropy S , and volume V to generally define temperature T at a constant volume:

$$T = \left(\frac{\partial E}{\partial S} \right)_V \quad (12)$$

and pressure P at a constant entropy:

$$P = - \left(\frac{\partial E}{\partial V} \right)_S \quad (13)$$

Because the derivative operand of both Eqs. (12) and (13) is the internal energy E , the total derivative of E can be written in terms of T and P :

$$dE = \left(\frac{\partial E}{\partial S} \right)_V dS + \left(\frac{\partial E}{\partial V} \right)_S dV = T dS - P dV \quad (14)$$

which indicates that E is an exact function of S and V , i.e., $E = E(S, V)$.

If the system consists of different molecular species, i.e., $k = 1, 2, \dots, n_K$, where n_K is the total number of species, then the total molecule number N is the sum of the number of molecules of all the species, i.e.,

$$N = \sum_k N_k = N_1 + N_2 + \dots + N_{n_K} \quad (15)$$

where, for example, N_2 is the total molecule number of species 2. Then, the infinitesimal change of E includes the effect of the particle exchange, using the chemical potential μ_k , as

$$dE = T dS - P dV + \sum_k \mu_k dN_k \quad (16)$$

In a closed system, the molecule numbers of multiple species can change simultaneously, keeping the total molecule number invariant. If the two systems in contact are at an equilibrium and molecules in the boxes can be exchanged, then the change of energy as per the number of exchanged molecules is equivalent to the chemical potential of the species. From Eq. (16), we can represent an extended version E as an exact function of S , V , and N_k :

$$E = E(S, V, \{N_k\}) \quad (17)$$

If a thermodynamic system is completely controlled by the three variables of N , V , and S , the system is said to be a microcanonical ensemble.

2.2.2. Helmholtz free energy in canonical ensemble

Since the temperature is a more convenient variable to measure than the entropy S , one can use the mathematical identity of $T dS = d(TS) - S dT$ to rewrite Eq. (16) as

$$dE = d(TS) - S dT - P dV + \mu_k dN_k \quad (18)$$

where the notation of the summation over the molecular species k , \sum_k is omitted for simplicity. The total derivative, $d(TS)$, is subtracted from both sides of Eq. (18) to have

$$dA = -S dT - P dV + \mu_k dN_k \quad (19)$$

where A is the Helmholtz free energy defined as

$$A = E - TS \quad (20)$$

If a thermodynamic system is completely described using T , V , and $\{N_k\}$ (for $k = 1, 2 \dots$), this ensemble is called canonical, and the Helmholtz free energy, $A(T, V, \{N_k\})$, is the representative energy function.

2.2.3. Enthalpy in isentropic-isobaric ensemble

Similar to how we derived the Helmholtz free energy, we start from the infinitesimal difference of the internal energy E of Eq. (16) using the mathematical identity of $P dV = d(PV) - V dP$ to have

$$dE = T dS - d(PV) + V dP + \mu_k dN_k \quad (21)$$

We add $d(PV)$ in the both sides of the above equation and obtain

$$dH = T dS + V dP + \mu_k dN_k \quad (22)$$

where

$$H(S, P, \{N_k\}) = E + PV \quad (23)$$

is defined as the enthalpy as a function of S , P , and $\{N_k\}$. Eq. (22) indicates that the enthalpy is independent of T unlike other energy functions (see the next sections for detailed discussion).

2.2.4. Thermodynamic potential in grand canonical ensemble

To have an ensemble that is independent of the number of particles, one can start from the infinitesimal change of Helmholtz free energy and use the identity of $\mu_k dN_k = d(\mu_k N_k) - N_k d\mu_k$ to have

$$dA = -S dT - P dV + d(\mu_k N_k) - N_k d\mu_k \quad (24)$$

Subtracting $d(\mu_k N_k)$ from each side of Eq. (24) gives

$$d\Phi = -S dT - P dV + N_k d\mu_k \quad (25)$$

where

$$\Phi(T, V, \{\mu_k\}) = A - \mu_k N_k \quad (26)$$

is defined as the thermodynamic potential, varying with respect to T , V , and μ_k . An ensemble described using μ , V , and T is called a grand canonical ensemble. The thermodynamic potential is further derived such that $\Phi = -PV$ if the thermodynamic system is homogeneous.

2.2.5. Gibbs energy in isothermal-isobaric ensemble

Finally, we replace $P dV$ in the infinitesimal change of A in Eq. (19) by $d(PV) - V dP$ to have

$$dG = -S dT + V dP + \mu_k dN_k \quad (27)$$

where

$$G(T, P, \{N_k\}) = A + PV = E - TS + PV \quad (28)$$

is defined as the Gibbs free energy varying with respect to T , P , and $\{N_k\}$. Now we assume that G is a homogeneous (i.e., linear) function of N_k such that $G \propto N_k$. In this case, the chemical potential of species k is represented in terms of T and P only as

$$\mu_k = \left(\frac{\partial G}{\partial N_k} \right)_{T, P} = \mu_k(T, P) \quad (29)$$

For the fixed number of particles, the infinitesimal change of the total chemical potential is

$$d\mu = \frac{1}{N} dG = -\bar{S} dT + \bar{V} dP \quad (30)$$

where $\bar{S} = S/N$ and $\bar{V} = V/N$ are the entropy and the volume per molecule, respectively, of the entire system. In practice, it is often convenient to use the entropy and energy per mole of molecules in engineering applications, but for basic study here we will keep using quantities divided by the number of molecules. For species k , we have the representation of the infinitesimal change in the chemical potential of species k :

$$d\mu_k = -\bar{S}_k dT + \bar{V}_k dP \quad (31)$$

Keeping the homogeneity assumption, the Gibbs energy function is written as a sum of products of the chemical potentials and the particle numbers:

$$G = \sum_k \left(\frac{\partial G}{\partial N_k} \right)_{T, P} N_k = \sum_k \mu_k(T, P) N_k \quad (32)$$

The thermodynamic potential is generally derived as $\Phi = A - \sum_k \mu_k N_k$ using the Legendre transformation from the previous section. If and only if the Gibbs energy function $G(= A + PV)$ is homogeneous such as Eq. (32), Φ can be further simplified to

$$\Phi = A - G = -PV \quad (33)$$

If the molecular interactions are strong, then Eq. (32) requires an extra coupling term proportional to $N_i N_j$, and Eq. (26) should be revisited as a general definition for Φ (see Section 1.3 for details). Dependences of the energy functions on thermodynamic variables in specific ensembles are summarized in **Table 1**.

Ensemble	Energy functions and relationships
Microcanonical (NVS)	Internal energy $E(N,V,S)$ $dE = TdS - PdV + \mu dN$
Canonical (NVT)	Helmholtz energy $A(N,V,T) = E - TS$ $dA = -SdT - PdV + \mu dN$
Grand canonical (μVT)	Thermodynamic potential $\Phi(\mu,V,T) = A - \sum_k \mu_k N_k$ $d\Phi = -SdT - PdV - Nd\mu$
Isothermal-isobaric (NPT)	Gibbs energy $G(N,P,T) = A + PV = \mu N$ $dG = -SdT + VdP + \mu dN$
Isentropic-isobaric (NPS)	Enthalpy $H(N,P,S) = E + PV$ $dH = TdS + VdP + \mu dN$

Table 1. Specific ensembles and associated energy functions.

2.3. Gibbs energy and anisothermal equilibrium

2.3.1. Thermodynamics variables: extensive and intensive

Consider a thermodynamic system in equilibrium, shown in **Figure 2**. The system is made by adding two identical systems, which are now in contact with each other. In this case, the seven thermodynamic variables change as follows:

- Additive (extensive): $N \rightarrow 2N$, $V \rightarrow 2V$, $S \rightarrow 2S$, and $E \rightarrow 2E$
- Nonadditive (intensive): $T \rightarrow T$, $P \rightarrow P$, and $\mu_k \rightarrow \mu_k$

As expected, the number of particles, volume, entropy, and energy are doubled by adding the two identical systems, and they are called *additive*. On the other hand, temperature, pressure, and chemical potential remain invariant, and they are called *nonadditive*.

The independence of the temperature to the system size can be understood using its basic definition of Eq. (12) as the change ratio of E to S as they are additive quantities. The pressure is defined in Eq. (13) as the negative ratio of changes of E to V . The chemical potential,

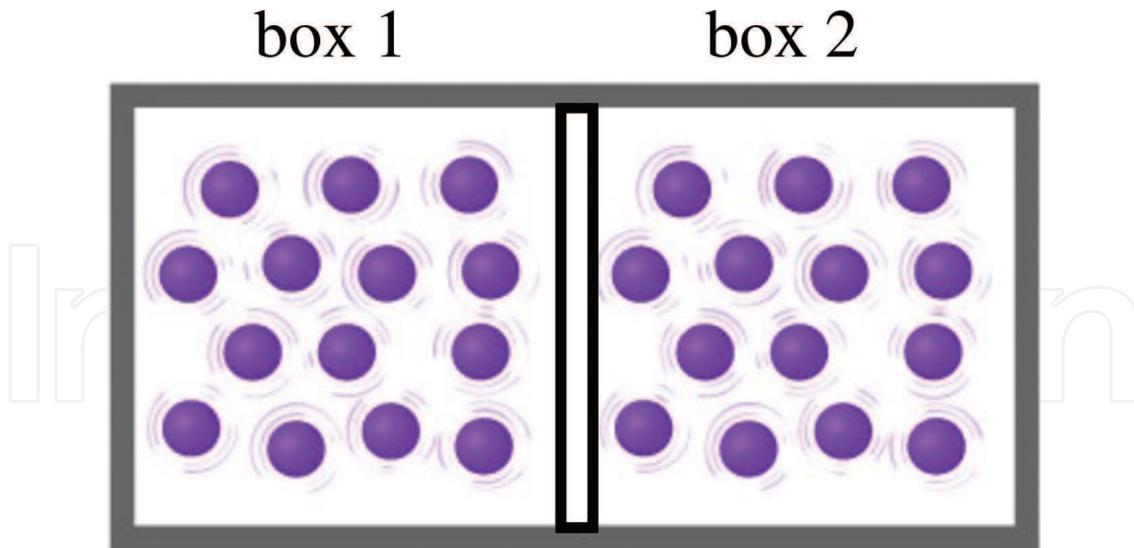


Figure 2. A closed system consisting of two identical boxes in a thermal equilibrium. The outer boundaries (gray) insulate mass and energy transfer from the environment, and each box has the same T , P , and N . If the central wall is removed, then the two identical systems are combined.

interpreted as the ratio of the internal energy change with respect to creation/disappearance of a molecule, must be independent of the number of molecules. Among the seven master variables in thermodynamics, additive quantities are E , S , N , and V , called *extensive*, and nonadditive ones are T , P , and μ_k , called *intensive*. Note that the intensive quantities are defined as ratios of extensive quantities.

In the previous sections, we reviewed the five standard ensembles with their energy functions derived from three independent variables as

- Internal energy $E(S, V, \{N_k\})$
- Helmholtz energy $A(T, V, \{N_k\})$
- Thermodynamic potential $\Phi(T, V, \{\mu_k\})$
- Enthalpy $H(S, P, \{N_k\})$
- Gibbs energy $G(T, P, \{N_k\})$

Among these energy functions, E , A , Φ , and H depend on at least one extensive variable, S or V . Gibbs energy function is the only one that depends on two intensive variables, T and P . Although G basically varies with N_k , if the system is homogeneous, the chemical potential $\mu_k(T, P)$ is independent to the number of particles N_k . In many engineering applications dealing with mass transfer phenomena, temperature and pressure are often maintained as (pseudo-) constants. Molecules and particles translate spatially from one location to other, or are converted to another species (i.e., created or annihilated through physical and chemical reactions). In this light, the Gibbs energy $G(T, P, \{N_k\})$ is the most convenient representation of the system undergoing mass and/or heat transfer in the isobaric and isothermal environment.

Enthalpy $H(S, P, \{N_k\})$ is often used to characterize mass transfer phenomena under an isobaric-isentropic environment between two different temperatures, allowing volume expansion or compression. H is mainly used to link two temperature-dependent quantities such as equilibrium constants of chemical reactions in the NPT ensemble because it does not vary with T .

2.3.2. Anisothermal equilibrium

Consider two heterogeneous systems in equilibrium. This is similar to the case shown in **Figure 2**, but boxes 1 and 2 are not thermodynamically identical. In each box, the internal energy is fully represented using N_i , V_i , and S_i of box i for $i = 1$ and 2. Assume their volumes do not change so that $dV_i = 0$. We express the infinitesimal change of the entropy from Eq. (16) as

$$dS_i = \frac{dE_i}{T_i} - \frac{\mu_i}{T_i} dN_i \quad (34)$$

If the total number of particles $N (= N_1 + N_2)$ is constant, we simply derive

$$\frac{\partial N_2}{\partial N_1} = \frac{\partial}{\partial N_1} (N - N_1) = -1 \quad (35)$$

In equilibrium, the total entropy $S = S_1 + S_2$ must be already maximized, having a constant value S_{\max} :

$$\frac{\partial S}{\partial N_1} = \frac{\partial S_{\max}}{\partial N_1} = 0 = \frac{\partial S_1}{\partial N_1} + \frac{\partial N_2}{\partial N_1} \frac{\partial S_2}{\partial N_2} = \frac{\partial S_1}{\partial N_1} - \frac{\partial S_2}{\partial N_2} \quad (36)$$

As the internal energy of each box, E_i , is kept invariant in Eq. (34), we derive

$$\frac{\partial S_1}{\partial N_1} = -\frac{\mu_1}{T_1} \quad \text{and} \quad \frac{\partial S_2}{\partial N_2} = -\frac{\mu_2}{T_2} \quad (37)$$

Substitution of Eq. (37) into (36) gives

$$\frac{\mu_1(T_1, P_1)}{T_1} = \frac{\mu_2(T_2, P_2)}{T_2} \quad (38)$$

which is simplified, if $T_1 = T_2$, to

$$\mu_1(P_1) = \mu_2(P_2) \quad (39)$$

for an isothermal environment. Note that Eqs. (38) and (39) consist of only intensive thermodynamic quantities. The chemical potential can be readily derived using Eq. (29) if the Gibbs energy is known.

3. Dilute solution

3.1. Chemical potentials

Now we consider a dilute (or weak) solution, in which the number of dissolved molecules in the solvent is much less than that of the solvent molecules. Without losing generality for environmental engineering purposes, we set water as the solvent. Gibbs free energy of the weak solution of a single solute species is [31]

$$G = N\mu_0(P,T) + nk_B T \ln\left(\frac{n}{Ne}\right) + n\psi(P,T) \quad (40)$$

where N and n are the numbers of solvent and solute molecules, respectively, μ_0 is the chemical potential of the pure solvent, and $\psi(P,T)$ is an arbitrary function for the chemical potential of the pure solute. Euler's number $e = 2.71828218\dots$ in the denominator of the logarithmic function on the right-hand side of Eq. (40) stems from Starling's formula, used for entropy calculations: $\ln n! \simeq n \ln n - n = n \ln(n/e)$

If the weak solution contains multiple species of solutes, then the Gibbs energy function is generalized as

$$G = N\mu_0(P,T) + k_B T \sum_i n_i \ln\left(\frac{n_i}{Ne}\right) + \sum_i n_i \psi_i(P,T) \quad (41)$$

One can easily calculate the chemical potentials for the solvent μ_w and solute μ_s as partial derivatives of G in Eq. (41) with respect to N and n , respectively. The former and latter are

$$\mu_w = \frac{\partial G}{\partial N} = \mu_0(P,T) - k_B T x \quad (42)$$

and

$$\mu_s = \frac{\partial G}{\partial n} = \psi(P,T) + k_B T \ln x \quad (43)$$

respectively, where $x (= n/N)$ is the number (or mole) fraction of solute molecules to solvent molecules. In a dilute solution, $x \ll 1$.

3.2. Osmotic pressure

Let's consider an isothermal system consisting of two boxes (1 and 2) of the same size in contact. Box 1 (and 2) has the solute mole fraction x_1 (and x_2) and pressure P_1 (and P_2). Since the total system is in isothermal equilibrium, the two boxes have the same temperature: $T_1 = T_2 = T$.

3.2.1. Using solvent chemical potential

In this thermodynamic environment, the chemical potentials of water in the two boxes should be equal to each other from Eq. (39):

$$\mu_{w,1} = \mu_{w,2} \quad (44)$$

$$\mu_0(P_1, T) - x_1 k_B T = \mu_0(P_2, T) - x_2 k_B T \quad (45)$$

We assume that the pressure difference is small enough to use the weak solution approximation without drastic thermodynamic changes but large enough to maintain the balance between the two boxes. Then, we expand $\mu_0(P_2, T)$ around P_1 using Taylor's series

$$\mu_0(P_2, T) \simeq \mu_0(P_1, T) + \left(\frac{\partial \mu_0}{\partial P} \right)_T \Delta P \quad (46)$$

at a fixed temperature T . We substitute Eq. (46) into Eq. (45) to obtain

$$\left(\frac{\partial \mu_0}{\partial P} \right)_T \Delta P = (x_2 - x_1) k_B T \quad (47)$$

where $\Delta P = P_2 - P_1$ and $\Delta x = x_2 - x_1$ are differences of pressure and solute mole fraction, respectively, between box 1 and 2. Using Eq. (31), the fundamental representation of the infinitesimal chemical potential, we replaced $\partial \mu_0 / \partial P$ with the volume per solvent, V/N . Then, the pressure difference ΔP is calculated as

$$\Delta P = k_B T \frac{N \Delta x}{V} = \mathcal{R} T \frac{\Delta n}{N_A V} \quad (48)$$

and finally denoted as

$$\Delta \pi = \mathcal{R} T \Delta C \quad (49)$$

using

$$\Delta n = N \Delta x = N x_2 - N x_1 = n_2 - n_1 \quad (50)$$

$$\Delta C = \Delta n / N_A = C_2 - C_1 \quad (51)$$

where n_i and $C_i (= n_i / N_A V)$ are the (absolute) number and the mole concentration of solutes in box i for $i = 1$ and 2 , N_A is Avogadro's number, and \mathcal{R} is the universal gas constant. Eq. (49) is called the van't Hoff equation,¹ which resembles the ideal gas law [33]. If the solution contains multiple species of solutes, Eq. (49) can be easily extended to

¹Jacobus H. van't Hoff received the first Nobel Prize in Chemistry in 1901 for the discovery of osmotic pressure in solutions. https://www.nobelprize.org/nobel_prizes/chemistry/laureates/1901/

$$\Delta\pi = \sum_i (C_{i,2} - C_{i,1}) \mathcal{R}T = \mathcal{R}T\Delta C \quad (52)$$

where $\Delta C = \sum_i (C_{i,2} - C_{i,1})$ is, in general, the difference of total mole concentration of solutes. If the total mass concentration of multiple species is known, then it should be carefully converted to total mole concentration using molecular weights of the contained species. The underlying assumptions of the van't Hoff equation (49) are summarized as follows:

1. The solute concentration is much smaller than the solvent concentration.
2. Temperature gradient between the two boxes is zero.
3. The Gibbs free energy of a dilute solution is described using the weak solution approach.

3.2.2. Using solute chemical potential

If the solvent chemical potentials of boxes 1 and 2 are equal, then the solute chemical potentials should be also the same:

$$\mu_{s,1} = \mu_{s,2} \quad (53)$$

which leads to

$$\psi(P_1, T) + k_B T \ln x_1 = \psi(P_2, T) + k_B T \ln x_2 \quad (54)$$

Using the same approximation for the pressure difference, we derive

$$-\left(\frac{\partial\psi}{\partial P}\right)_T \Delta P = k_B T \Delta(\ln x) \quad (55)$$

$$= k_B T \ln\left(\frac{x_2}{x_1}\right) \quad (56)$$

where $\Delta \ln x = \ln x_2 - \ln x_1$ is the logarithmic difference between concentrations in two boxes. Eq. (56) can further be approximated as follows:

$$-k_B T \ln\left(\frac{x_2}{x_1}\right) = -k_B T \ln\left(1 + \frac{\Delta x}{x_1}\right) \simeq -k_B T \frac{\Delta x}{x_1} \quad (57)$$

We treat the negative derivative of ψ with respect to P as the volume per each solute molecule, i.e.,

$$-\left(\frac{\partial\psi}{\partial P}\right)_T = \frac{V}{n_1} \sim \frac{V}{n_2} \sim \frac{V}{\bar{n}} \quad (58)$$

where $\bar{n} = (n_1 + n_2)/2$, implicitly assuming $N \gg n_i \gg \Delta n$ for $i = 1, 2$. The pressure difference is then calculated as

$$\Delta P = \frac{n_1}{V} \frac{\Delta x}{x_1} k_B T = \frac{n_1/N}{x_1} \frac{N \Delta x}{V} k_B T = 1 \cdot \frac{\Delta n}{V} k_B T = \frac{\Delta n/N_A}{V} \mathcal{R} T \quad (59)$$

which reduces to the identical result of Eq. (49):

$$\Delta \pi = \mathcal{R} T \Delta C \quad (60)$$

The same result can be obtained in a slightly more mathematical way by directly using Eq. (55):

$$\Delta P = \frac{k_B T}{-(\partial \psi / \partial p)_T} \left(\frac{d \ln x}{dx} \right) \Delta x \quad (61)$$

$$= \frac{k_B T}{-(\partial \psi / \partial p)_T} \frac{\Delta x}{x} \quad (62)$$

where

$$\Delta(\ln x) \simeq \left(\frac{d \ln x}{dx} \right) \Delta x = \frac{\Delta x}{x} \quad (63)$$

is used. If Δx is finite, a similar approximation can be suggested:

$$\Delta(\ln x) = \left(\frac{\Delta \ln x}{\Delta x} \Delta x \right) = \frac{\Delta x}{\langle x \rangle_{\ln}} \quad (64)$$

where

$$\langle x \rangle_{\ln} = \frac{\Delta x}{\Delta \ln x} \quad (65)$$

is the logarithmic average of the solute mole fraction across the membrane interior. Employing Eq. (58) and $\Delta x/x = \Delta C/C$, we confirm that the osmotic pressure of the dilute concentration is

$$\Delta \pi = \frac{\mathcal{R} T}{-N_A (\partial \psi / \partial p)_T} \frac{\Delta x}{x} = \mathcal{R} T \left(\frac{n}{N_A V} \right) \frac{\Delta C}{C} = \mathcal{R} T \Delta C \quad (66)$$

In this section, we mathematically proved that the osmotic pressure (of Eqs. (49), (60), and (66)) is valid for dilute solution consisting of weakly interacting molecules. Without losing generality, the absolute value of the osmotic pressure can be expressed as (similar to the ideal gas law)

$$\pi = CRT \quad (67)$$

Finally, it is worth noting that in Eq. (58), *the negative sign of the partial derivative indicates that the gradients of solvent and solute concentrations have opposite signs*. If the middle wall between the two boxes in **Figure 3** is partially removed, then solvent and solutes will diffuse in opposite

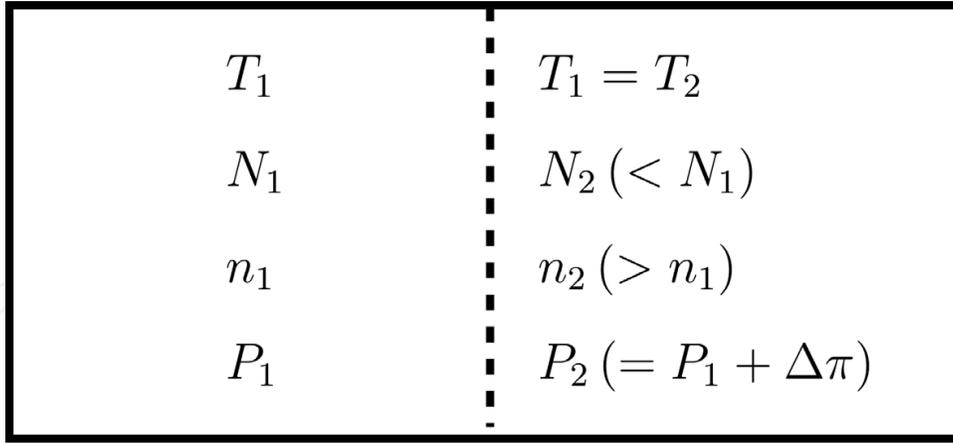


Figure 3. Osmotic pressure schematic: two boxes separated by the semipermeable wall in the isothermal environment.

directions. This should be treated in principle as a binary diffusion of two species (i.e., solvent and solute) by exchanging their positions.

4. Solution-diffusion model revisited

4.1. Solvent (water) transport

For pressure-driven membrane processes such as RO and NF, the applied pressure should overcome the osmotic pressure difference across the membrane. In feed and permeate solutions, salts are dissolved as solutes in the solvent water. The hydraulic pressure generates solvent flow through the membrane, which may contribute to solute transport through the membrane surface. Water molecules, however, dissolve as solutes in the membrane material (as solvent). Due to the high density of the membrane, water molecules can migrate via diffusion from a higher concentration region to a lower concentration region. This normal diffusion is reversed by applying hydraulic pressure to the feed solution with a high concentration such as seawater. Water permeation through a RO membrane can be pictured as diffusion driven by the external hydraulic pressure, which allows us to neglect convective transport of solutes through the membrane. The phenomenological phase of water in the membrane leads to solute transport as Fickian, which is also closely related to the osmotic pressure gradient between two subsystems. The above-mentioned mechanisms are included in *solution-diffusion* model, proposed by Lonsdale et al. [30]. An extensive overview of RO models can be found elsewhere [34–39].

Consider a semipermeable membrane of thickness δ_m , with high and low concentrations on two sides. The solvent flux through the membrane is assumed to be Fickian [40, 41]:

$$J_w = -D_w \frac{dC_w}{dx} \quad (68)$$

where C_w is the concentration of water *dissolved in the membrane*. Assuming that the dissolved water in the membrane material can be treated as a *Henrian* solution, the chemical potential of the pure water (in the membrane solvent) is

$$\mu_w = \text{constant} + \mathcal{R}T \ln C_w \quad (69)$$

In this model, the underlying assumptions are:

1. The water and solute molecules dissolve into a membrane material.
2. The solution is considered as Henrian for water.
3. The feed and permeate streams are immiscible with the membrane.

Substitution of Eq. (69) into Eq. (68) gives

$$J_w = -D_w \frac{C_w}{\mathcal{R}T} \frac{d\mu_w}{dx} \approx \frac{D_w C_w}{\mathcal{R}T \delta_m} \Delta\mu_w \quad (70)$$

where $\Delta\mu_w$ is the transmembrane difference of μ_w at a constant temperature T , which can be written as

$$\Delta\mu_w = \int \frac{\partial\mu_w}{\partial C_s} dC_s + \bar{V}_w \Delta P \quad (71)$$

where C_s is the solute concentration. In the previous section, we proved that the chemical potential difference between two subsystems should vanish in the isothermal equilibrium (i.e., $\Delta T = 0$): $\Delta\mu_w = 0$. In this case, the transmembrane pressure difference is equal to the osmotic pressure difference, i.e., $\Delta P = \Delta\pi$, which gives

$$\int \frac{\partial\mu_w}{\partial C_s} dC_s = -\bar{V}_w \Delta\pi \quad (72)$$

Then, Eq. (71) is simplified to

$$\Delta\mu_w = \bar{V}_w (\Delta P - \Delta\pi) \quad (73)$$

Substitution of Eq. (73) into Eq. (70) provides

$$J_w = A(\Delta P - \Delta\pi) \quad (74)$$

which is the governing equation of solvent transport through the membrane as a medium in which water and solutes can dissolve. Here, A is the water permeability through the membrane:

$$A = \frac{D_w C_w \bar{V}_w}{\mathcal{R}T \delta_m} \quad (75)$$

which is a characteristic value of the membrane. It is challenging to predict or measure the diffusion coefficient D_w and dissolved concentration C_w of water molecules in the membrane material. Therefore, the water permeability A is often experimentally estimated by a linear regression plot of J_w versus ΔP using fresh water as a solute-free feed solution.

4.2. Solute transport

The solute transport through the membrane is also assumed to follow Fick's law:

$$J_s = -D_s \frac{dC_s}{dx} \simeq D_s \frac{\Delta C_s}{\delta_m} \quad (76)$$

where C_s and D_s are the concentration and diffusivity of solutes *dissolved* in the membrane, respectively, and ΔC_s is the solute concentration difference across *the membrane interior*. Similarly to C_w , C_s is hard to measure. Therefore, ΔC_s is assumed to be proportional to that between membrane surfaces ΔC_m . The partition coefficient K is then defined as

$$K = \frac{\Delta C_s}{\Delta C_m} \quad (< 1) \quad (77)$$

where ΔC_m is often approximated as the difference between feed concentration C_f and permeate concentration C_p in the RO processes. Substitution of Eq. (77) into Eq. (76) provides

$$J_s = B \Delta C_m \quad (78)$$

where

$$B = \frac{D_s K}{\delta_m} \quad (79)$$

is the solute permeability through the membrane. Note that B conventionally has the same dimension as J_w . Similarly to A , B can be macroscopically measured by independent experiments, providing a J_s versus ΔC_m graph. The slope of the graph, estimated using linear regression, is equal to B .

5. Thermodynamic irreversibility of filtration

A thermodynamic system has three types: open, closed, and isolated. In the open system, mass and heat can pass in and out of the system in contact with the environment. Only heat can be transferred between the closed system and the environment, and neither mass nor heat can be exchanged in the isolated system. Rigorously saying, all the filtration processes are open systems, having entering feed streams to be treated. Temperature gradients across the membrane are often negligible in the pressure- or osmosis-driven filtration processes, but significant in thermal membrane processes such as membrane distillation processes [42–45]. To address the open filtration processes, nonequilibrium statistical mechanics (NESM) should

be used [46–48]. To the best of our knowledge, the NESM still burgeons in pure theoretical physics. Therefore, general solutions for irreversible engineering processes are barely found. The minimum condition for us to use equilibrium filtration theory is that the filtration system is already in a steady state, in which no physical quantities vary explicitly with respect to time, i.e., mathematically,

$$\frac{\partial[\]}{\partial t} = 0 \quad (97)$$

where [] can hold any variables associated to the filtration system. The steady state is, in principle, far away from static equilibrium. Note that the osmotic pressure is derived from a pure equilibrium state, especially for the isobaric-isothermal ensemble. This implies that the solution-diffusion model becomes less accurate if fluid flows in the membrane channels are fast enough or almost turbulent.

To investigate the intrinsically nonequilibrium filtration processes, the irreversible thermodynamic models were developed using the Onsager² reciprocal theorem [49]. Kedem and Katchalsky represented the local dissipation rate of free energy per unit volume as *dissipation function* for isothermal, nonelectrolyte systems in a steady state [50]:

$$\phi = \sum_{k=1}^n \vec{J}_k \cdot \nabla(-\mu_k) > 0 \quad (80)$$

for species k , having a constant flux \vec{J}_k . In the irreversible (i.e., nonequilibrium) process, entropy must increase and therefore the dissipation rate is positive-definite, i.e., $\phi > 0$. The dissipation function for RO is

$$\phi = J_v \Delta P + J_D \Delta \pi \quad (81)$$

where J_v and J_D are the total volumetric flux and the solute velocity relative to the solvent velocity, respectively. One can write

$$J_v = L_{11} \Delta P + L_{12} \Delta \pi \quad (82)$$

$$J_D = L_{21} \Delta P + L_{22} \Delta \pi \quad (83)$$

where L_{ij} are coupling coefficients of the phenomenological fluxes, J_v and J_D . In order to satisfy Eq. (81), the following two conditions must be met

$$L_{11}, L_{22} > 0 \quad (84)$$

and

²Lars Onsager received the Nobel Prize in Chemistry in 1968 for the discovery of the reciprocal relations in the fundamental thermodynamics of irreversible processes. http://www.nobelprize.org/nobel_prizes/chemistry/laureates/1968/

$$L_{11} L_{22} \geq L_{12} L_{21} = L_{12}^2 \quad (85)$$

where $L_{12} = L_{21}$.

After some theoretical steps, Kedem and Katchalsky [50] derived

$$J_v = L_{11} (\Delta P - \sigma \Delta \pi) \quad (86)$$

$$J_s = \bar{C}_s (1 - \sigma) J_v + \omega \Delta \pi \quad (87)$$

where \bar{C}_s is the logarithmic average of concentrations on the two membrane sides, $\sigma = -L_{12}/L_{11}$ assuming $L_{11} > 0$ and $L_{12} < 0$, and

$$\omega = \bar{C}_s \frac{L_{11} L_{22} - L_{12}^2}{L_{11}} = \bar{C}_s (L_{22} - \sigma |L_{12}|) \quad (88)$$

Here, σ is defined as the “filtration coefficient,” representing the solute rejection property. Kedem and Katchalsky [50] interpret the physical meaning of σ as follows: when $\sigma = 1.0$, the membrane is completely impermeable to solute and rejection is 100%, and when $\sigma = 0.0$, the membrane is completely permeable to solute and rejection is zero. It is worth noting that the irreversible thermodynamic theory includes the solution-diffusion model as a special case. If $\sigma = 1.0$, then Eqs. (86) and (87) reduce to

$$J_v = L_{11} (\Delta P - \Delta \pi) \rightarrow A (\Delta P - \Delta \pi) \quad (89)$$

$$J_s = \bar{C}_s (L_{22} - |L_{12}|) \Delta \pi \rightarrow B \Delta C \quad (90)$$

where $L_{11} = A$ and $B = \omega \Delta \pi / \Delta C$, assuming the osmotic pressure is linearly proportional to the solute concentration.

In our opinion, $\sigma = 1$ can be interpreted in a different way. Because the unity σ in Eqs. (86) and (87) indicates that the effect of $\Delta \pi$ is maximized, the thermodynamic state of the membrane surface is quite close to the static equilibrium state. The solvent flux can be considered as the *barometric diffusion of water* as J_v increases with ΔP , overcoming $\Delta \pi$ across the membrane. The solute flux in this case is purely Fickian, which is dominated by only $\omega \Delta \pi$ ($\propto \Delta C$) in Eq. (87). The limiting value of $\sigma \rightarrow 1$, however, does not guarantee the perfect rejection of solutes because it does not satisfy $J_s = 0$ in Eq. (90). Knowing $L_{12} < 0$, one can rewrite Eq. (85) to give

$$L_{22} - |L_{12}| \geq \frac{L_{12}^2}{L_{11}} + L_{12} = \sigma^2 L_{11} + L_{12} = L_{11} \sigma (\sigma - 1) \quad (91)$$

which indicates that the solute flux J_s may vanish if $\sigma = 0$ or 1. Here, we have to discard $\sigma = 0$ because J_s in Eq. (87) reaches its maximum at $\sigma = 0$. Then, the condition $\sigma = 1$ applied to Eq. (91) must be only a necessary condition for $J_s = 0$. The inequality relationship in Eq. (91)

indicates that the perfect rejection can be achieved if $L_{22} - |L_{12}| = 0$ in addition to $\sigma = 0$. In membrane separations, the perfect rejection is related not only to the thermodynamic state of the membrane surface, but also to the specific membrane materials having salt rejecting capabilities.

Furthermore, variations of J_v and J_s with respect to σ can be investigated by calculating

$$\frac{1}{L_{11}} \frac{\partial J_v}{\partial \sigma} = -\Delta\pi \quad (92)$$

$$\frac{1}{\bar{C}_s L_{11}} \frac{\partial J_s}{\partial \sigma} = -[\Delta P + \Delta\pi] + \Delta\pi\sigma \quad (93)$$

and substitution of Eq. (92) into Eq. (93) gives

$$\frac{1}{\bar{C}_s L_{11}} \frac{\partial J_s}{\partial \sigma} - \sigma \Delta\pi = \frac{1}{L_{11}} \frac{\partial J_v}{\partial \sigma} - \Delta P \quad (94)$$

which is valid for an arbitrary σ between 0 and 1. Eq. (92) indicates that J_v monotonously decreases with respect to σ . If the filtration system is in a transient, nonequilibrium state far from the pure static equilibrium, the volumetric flux J_v must be higher than that in the quasiequilibrium state. The left-hand side of Eq. (93) is $-\Delta P$ at $\sigma = 1$ and $-\Delta P + \Delta\pi$ at $\sigma = 0$: as σ decreases, the magnitude of $\partial J_s / \partial \sigma$ increases.

Overall, σ can be physically interpreted not only as the filtration coefficient, but also as the equilibrium coefficient. When $\sigma \rightarrow 1$, the effect of the osmotic pressure difference reaches its maximum of the quasiequilibrium state, but the zero solute flux is not automatically guaranteed. The perfect rejection is achieved if the additional condition $L_{22} = |L_{12}|$ is satisfied, which is, however, independent of σ . The difference of σ indicates how much the filtration system is phenomenologically close to the static equilibrium. On the other side, if $\sigma \rightarrow 0$, then the filtration system can be in a steady state, but it is far from the static equilibrium. J_v and J_s approach their theoretical maximum values, and the solute transport is significantly influenced by convection. Although σ is a fundamentally and practically important parameter, to the best of our knowledge, there are no standard theories to directly predict σ . This is because the irreversible thermodynamic model relaxes the equilibrium restriction, but the NESM has not been fully developed yet.

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