



# Gibbs energy role in fresh and salt water mixing



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## HIGHLIGHTS

- The energy of osmotic systems is produced due to thermal energy of the environment.
- The reversible mixing of feed and draw solutions is followed by mixture cooling.
- The friction in the membrane should not lead to work losses.
- All theoretical calculations in terms of the Gibbs energy are still valid.

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## ABSTRACT

It is well-known that the process of mixing two solutions of different concentrations may produce energy. The change in Gibbs energy upon mixing is believed to be the source of energy. However, the change in the Gibbs energy is independent of the way of mixing, i.e., irreversible (without work production) or reversible (with the obligatory production of work). The Gibbs energy cannot be an energy source for producing work. The entropy of mixing solutions and the environment has been considered to elucidate the role of the Gibbs energy in the reversible process. It is shown that the environment takes active part in energy production. The Gibbs energy may be a mathematical means for performing thermodynamic calculations.

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## 1. Introduction

When mixing fresh and salt water, osmotic processes are taken as promising for producing clean energy [1–6]. The energy produced may be stored as a potential energy in the environment. It is widely held that the energy produced by mixing two solutions of different concentrations is due to the Gibbs energy [1–6]. The environment is not commonly considered. The goal of the present paper is to reveal the role of the Gibbs energy in energy production upon solution mixing with regard to the processes occurring in both solutions and the environment. To this end, we consider the change in entropy upon mixing for both the environment and solutions.

## 2. Irreversible mixing

We consider only the mixing of ideal solutions which occurs at constant temperature and pressure. In ideal solutions, all molecules are of the same size and the interactions between the molecules of different

types are also the same [7]. It is well-known [7] that the irreversible mixing (without work production) of two ideal solutions fails to cause either heat emission or the change in volume. Hence,

$$\Delta H(\text{mixing}) = 0, \quad (1)$$

$$\Delta V(\text{mixing}) = 0. \quad (2)$$

Upon mixing, the entropy increases and the Gibbs energy decreases

$$\Delta S(\text{mixing}) > 0, \quad (3)$$

$$\Delta G(\text{mixing}) = \Delta H(\text{mixing}) - T\Delta S(\text{mixing}) = -T\Delta S(\text{mixing}) < 0. \quad (4)$$

The absence of both heat emission and the change in volume upon mixing indicates that the solutions of different concentrations have no potential energy to perform work.

The decrease in the Gibbs energy upon mixing means that the Gibbs energy is not conserved. Thus, it is not the true energy [8–10]. Therefore, the role of the Gibbs energy in energy production upon mixing calls for further studying.

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### 3. Reversible mixing

In this section, we are going to consider reversible processes as a model to which the real processes, producing useful work, may tend. Strictly speaking, there are no reversible processes. However, a series of processes, in particular the osmotic ones, may produce useful work with a fairly high efficiency. It is worth noting that only the reversible processes are always followed by production of the maximal, useful work [11,12].

The work of reversible processes can be produced by special instruments. In osmotic systems, the semipermeable membranes serve as these. Using the semipermeable membranes in the system has no effect on the change in volume, enthalpy, entropy, and the Gibbs energy upon solution mixing. The change in these values is independent of process character, reversible or irreversible, because all of these values are the state functions.

The absence of the change in entropy for the environment and solutions is an important characteristic of the reversible process

$$\begin{aligned} \Delta S(\text{mixed solutions} + \text{environment}) \\ = \Delta S(\text{mixed solutions}) + \Delta S(\text{environment}) = 0, \end{aligned} \quad (5)$$

since only the fulfillment of condition (5) provides the reversibility of the process. As follows from Eq. (5)

$$\Delta S(\text{environment}) = -\Delta S(\text{mixing}) < 0. \quad (6)$$

As the temperature of the environment and solutions is uniform, the entropy of the environment may change only upon thermal energy transfer from the environment to the mixture of solutions

$$\Delta S(\text{environment}) = \Delta H(\text{environment})/T < 0. \quad (7)$$

Since the temperature of the mixture of solutions remains uniform upon this transfer of thermal energy, in virtue of the law of energy conservation, the transferred thermal energy must produce work

$$\Delta H(\text{environment}) = w'_{\text{useful}}, \quad (8)$$

where  $w'_{\text{useful}}$  is the maximal useful work of the reversible process. From Eqs. (4), and (6)–(8) we find that

$$w'_{\text{useful}} = \Delta G(\text{mixing}) = \Delta H(\text{environment}). \quad (9)$$

Thus, the useful work of the osmotic, reversible process is equal to the change in the Gibbs energy upon mixing but is performed due to the thermal energy of the environment.

The useful work in the reversible, osmotic system is performed due to the tendency of the system to the equilibrium state against the applied pressure, equal to the osmotic one. To achieve equilibrium, water from feed solution penetrates draw solution through a membrane. As a result, the volume of draw solution increases and the work is performed which is equal to the product of pressure difference by volume of penetrating solution. Work production requires energy sources. However, the system has no sources other than the thermal energy of solutions. Therefore, the water, performing work, is cooled upon penetration into the draw solution and cools it. In this case, a minor difference appears in the temperatures of the draw solution and the environment. Thereafter, the mixture temperature is restored due to heat transfer from the environment. In the reversible system, the processes are usually infinitely slow. It is assumed then that in the combined system (solutions + environment), the temperature is always uniform. The environment serves as a thermostat of extremely large heat capacity.

Note that this description of work production due to the heat of the environment is in fair agreement with the second law of thermodynamics. The law prohibits work production in the process which results only

in heat absorption from a reservoir and in complete conversion of this absorbed heat into work [11, p. 94]. In reversible osmotic systems, the absorption of heat from the environment (reservoir) is connected not only with work production but also (which is of high importance) with the process of concentration variations. Therefore, the second law is not violated.

It might be surprising that the useful work is performed due to the thermal energy of the environment whereas the amount of work is calculated in terms of the change in the Gibbs energy upon solution mixing without involvement of the environment. The point is that calculations according to Eq. (9) use the thermodynamic parameters only of the initial and final states of the system of solutions. A concrete realization of the reversible process of mixing does not describe Eq. (9) and may be realized by various methods including the active participation of the environment [13] (which is demonstrated above). No matter what is the way the reversible process follows, the value of the maximal useful work will be unambiguously calculated from Eq. (9). Therefore, the results of theoretical studies e.g., [1–6], using the Gibbs energy to carry on thermodynamic calculations upon description of osmotic phenomena, cannot undergo substantial changes. Minor corrections in calculations, related to the change in temperature upon mixing, are of no essence because of a small change in temperature.

### 4. Estimation of temperature variations upon reversible mixing

Let us estimate the change in mixed water temperature due to the reversible process of mixing which results in reversible work. Solutions are taken as ideal. The reversible mixing is followed by the cooling of mixed water whose temperature may increase to the ambient one upon heat transfer. It is assumed then that the heat transfer from the environment to water solutions is highly slow which allows one to estimate the maximal cooling. Therefore, only the resulting mixture of draw and feed solutions is first cooled.

Calculate now the change in temperature upon reversible mixing of one liter of the draw solution with several moles ( $N_1$ ) of the feed solution. One liter of the draw solution contains 55.5 mol of ( $N_0$ ) molecules among which there are  $n$  moles of ions. We assume that  $n \approx 1.2 M$  [4].

The process of mixing causes the change in the Gibbs energy of both water and dissolved ions.

$$\Delta G(\text{mixing}) = \Delta G(\text{mixing, ions}) + \Delta G(\text{mixing, water}). \quad (10)$$

It is worth noting that since the Gibbs energy is a state function, its variations are independent of process character, i.e., reversible or irreversible, with or without work production.

For ions, the change in the Gibbs energy is of the form

$$\begin{aligned} \Delta G(\text{mixing, ions}) \\ = n \left( \mu_{\text{ions}}^{\circ} + RT \ln \frac{n}{N_0 + N_1} \right) - n \left( \mu_{\text{ions}}^{\circ} + RT \ln \frac{n}{N_0} \right), \end{aligned} \quad (11)$$

where  $\mu_{\text{ions}}^{\circ}$  is a standard, chemical ion potential in water,  $\frac{n}{N_0 + N_1}$  is a molar fraction of ions in the formed mixture of draw and feed solutions, and  $\frac{n}{N_0}$  is a molar fraction of ions in the initial draw solution. Assuming that  $n \ll N_0$ , we get

$$\Delta G(\text{mixing, ions}) \approx -nRT \ln \alpha, \quad (12)$$

where  $\alpha$  is the coefficient of dilution equal to

$$\alpha = \frac{N_0 + N_1}{N_0}. \quad (13)$$

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