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MECHANICAL ENERGY FROM SALINITY GRADIENTS

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Abstract

After a brief discussion of the conversion from chemical to mechanical energy by direct osmosis or by vapor pressure differences, this paper deals with a preliminary approach to energy conversion of salinity gradient by the kinetical response to the chemical free energy variation, between fresh-water and the saline solution.

1.-Introduction

The possibility of energy conversion by salinity gradients is, in general, based on the process known as direct osmosis [1-6].

When a semi-permeable membrane separates two compartments A and B, the first one with pure water and the other one with a solution of salts in a solvent as water, it is only possible the transport of the solvent from A to B, but not the solutes from B to A. The "thermodynamic force" that produces the flux of solvent is the difference of chemical energy (or free energy) amongst the pure water and the water in the saline solution. Spontaneous processes go in the sense of the diminution of chemical energy. In the case under consideration, free energy of pure water is greater than the energy of the water in the solution in compartment B, at the same temperature. When initially the mechanical pressure is the same in both compartments, the system is not in thermodynamical equilibrium. The relaxation to equilibrium occurs by means of the solvent transport from A to B; the pressure increases in B with respect to A until reaching a value of P_{os} named "osmotic pressure". Compartment A can contain instead of pure water a solution of the same salts with a smaller concentration than that contained in compartment B.

There are also some papers that propose the salinity gradient energy conversion by means of the vapor pressure differences between two compartments, one with freshwater and the other with a saline solution, at the same temperature.

In the first part of this paper, the process of direct osmosis with semi-permeable membranes is described. The last part deals with the principal purpose of this paper: the potential use of the free energy gradient in an interface between two solutions, for obtaining an unsteady flow of kinetic energy that can be used in engineering applications.

2.- Chemical potential and osmotic pressure of solutions

If n is the number of molecules of solute mixed with N molecules of solvent, in a weak solution of concentration $c = n/N$ where $n/N \ll 1$, the chemical potential of the solvent in the given solution of concentration c is [7],

$$\mu = \mu_0(P, T) - kcT \quad (1)$$

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where μ_0 is the chemical potential of the pure solvent at the temperature T and pressure P .

k is the Boltzmann constant, $k=1,38 \cdot 10^{-23}$ J/°K

It must be remembered that chemical potential μ is associated with the number of molecules in any of the expressions of the thermodynamical potential, internal energy U , thermal function or enthalpy W , Hemholtz free energy F , and Gibbs free energy G . The last two are

$$\mu = \left(\frac{\partial F}{\partial N} \right)_{T,V} = \left(\frac{\partial G}{\partial N} \right)_{P,T} \quad (2)$$

Moreover,

$$G = N\mu \quad (3)$$

For thermodynamical equilibrium, the chemical potential of the solvent must be equal in both compartments A and B described in the Introduction. Chemical potentials of solute are not equal because solute molecules can not go through the semi-permeable membrane. Then,

$$\mu_0(P_1, T) - kc_1T = \mu_0(P_2, T) - kc_2T \quad (4)$$

where c_1 and c_2 are the concentrations of solute in compartments A and B respectively.

For weak solutions, μ_0 can be developed in a series, retaining the first two terms [7],

$$\mu_0(P_2, T) = \mu_0(P_1, T) + \Delta P \frac{\partial(\mu_0)}{\partial P} \quad (5)$$

From (1)

$$\Delta P \frac{\partial(\mu_0)}{\partial P} = k(c_2 - c_1)T \quad (6)$$

But, $\frac{\partial(\mu_0)}{\partial P} = v$, the molecular volume of the pure solvent

$$\Delta P = \frac{(c_2 - c_1)kT}{v} \quad (7)$$

If $c_1=0$, and N is the number of solvent molecules,

$$\Delta P = \frac{c_2 N k T}{V} \quad (8)$$

or

$$\Delta P = \frac{nkT}{V} \quad (9)$$

where n is the number of the solute molecules, and ΔP is the so called osmotic pressure.

This expression is the Van't Hoof formula. It resembles the ideal gas equation. As the solution is weak, the V volume coincides with the total volume of the solution. This formula can be applied to all weak solutions, independent of the solute and solvent molecules.

Direct osmosis converts chemical energy into mechanical energy. Power can be expressed as the product of two conjugated quantities, one extensive and the other intensive. In this case, the water flowrate and the osmotic pressure. Although ΔP can attain high values, the water flowrate through the semi-permeable membranes is very low. For example, with fresh water in one side and sea water in the other, the osmotic pressure is around 24 atm, while the water flow-rate is around 4 cm^3 for second and 1 m^2 of membrane area. This limitation leads to design systems from salinity gradients without the use of semi-permeable membranes. In the inverse process known as reversed osmosis, some energy is spent and is used, for example, in desalination of seawater.

The energy conversion by salinity gradients without membranes taking into account the lowering of vapor pressure in solutions is shown in references [8,9].

3.- Flow of kinetic energy due to free energy variation

Direct osmosis is a slow, a quasi-equilibrium evolution due to the membrane permeability. A spontaneous process at constant temperature and pressure can be treated using the Gibbs free energy

$$G = W - TS \quad (10)$$

In the chemical -physics process of interfacing a pure solvent and a weak solution of a certain solute in the same solvent, at constant temperature, the process is defined by the change of G .

In a fluid, the expression of the energy flux contains two local temporal variations corresponding to the kinetic energy and to the internal energy [10]. In this case, we are interested in the first one, which provides a relation between mechanical and thermodynamical functions.

$$\frac{\partial \left(\frac{\rho v^2}{2} \right)}{\partial t} = -\frac{v^2}{2} \cdot \text{div}(\rho \bar{v}) - \rho \bar{v} \cdot \nabla \left(w + \frac{v^2}{2} \right) + \rho T \bar{v} \cdot \nabla s \quad (11)$$

where v is the fluid velocity, T is the absolute temperature, w is the enthalpy per unit mass, s is the unit mass entropy and ρ is the density.

By the continuity equation

$$\frac{\partial \rho}{\partial t} + \text{div}(\rho \bar{v}) = 0 \quad (12)$$

and reordering the equation (11), results

$$\frac{d}{dt}\left(\frac{\rho v^2}{2}\right) = \frac{\partial}{\partial t}\left(\frac{\rho v^2}{2}\right) + \bar{v} \cdot \nabla\left(\frac{\rho v^2}{2}\right) = \frac{v^2}{2} \frac{\partial \rho}{\partial t} - \rho \bar{v} \nabla w + \rho \bar{v} T \nabla s \quad (13)$$

Neglecting, for weak solutions, the local temporal variation of ρ and taking into account (11), it can be written

$$\frac{d}{dt}\left(\frac{\rho v^2}{2}\right) = -\rho \bar{v} \nabla(w - Ts) = -\rho \bar{v} \nabla(g) \quad (14)$$

If there is some gradient of saline concentration, there will be a free energy gradient and consequently a kinetic variation when pure water is moved with velocity v and temperature T . One can think in a channel for pure water, another for the saline solution in the same direction but separated by a length L for mixing and producing some gradient concentration when two sluices or ports are raised.

A similar natural system of a great scale occurs when a river flows to an ocean.

In this example, there is a negative change of free energy g from solvent to solution, so $(-\nabla g)$ is in the same sense of the velocity. The scalar product is positive and there is an increment of kinetic energy. This kinetic variation can be transformed in a pressure rise. Owing to a degree of irreversibility occurring in the solution process, the mechanical work available is smaller than the theoretical (maximum) one calculated by means of the pressure and the flow-rate of the unsteady flow.

The initial kinetic change will be calculated with an adopted initial velocity v_0 , neglecting any diffusion of salts, using (14) and the interval of 1 second.

The chemical free energy gradient is calculated by the quotient $\frac{\Delta g}{\Delta l}$, adopting some value for Δl .

Then, from (3) and (1),

$$\Delta G = N \Delta \mu = -N k T c \quad (15)$$

Per unit mass,

$$N = \frac{N_a}{M_w} \quad (16)$$

where N_a is the Avogadro number and $M_w = 18$ is the molecular weight of water,

$$\frac{\Delta v^2}{2} = \frac{N_a}{M_w} k T c v_0 \frac{\Delta g}{\Delta l} \Delta t \quad (17)$$

$N_a = 6,02 \cdot 10^{26} \text{ (kg mol)}^{-1}$

The chemical potential of the solute is not taken into account.

From (17), the increment $\Delta v^2/2$ and an equivalent water height $\Delta H_{\max} = \frac{\Delta v^2}{2g}$ for a 100% of conversion efficiency from chemical to mechanical energy. It can be expected that the efficiency of

chemical-mechanical conversion depends on the initial velocity v_0 , owing to dissipation phenomena such as turbulence and diffusion, smaller output for greater velocities. The values are indicated in the table for an efficiency of 1%.

The expression (17) was derived from (11) pertaining to the field of fluid mechanics; it has the same root that the one considered in direct osmosis, that is, the difference of chemical potentials between the pure solvent and a weak solution of a salt in the same solvent, but with an interesting consequence that (17) allows to obtain the kinetical energy variation and not only the quasi-equilibrium osmotic over-pressure.

The concentration c' in units of Kg of solute (Cl Na) for a Kg of solvent for each value of c can be calculated by means of

$$c' = \frac{M_{sol}}{M_{solv}} c = \frac{M_{ClNa}}{M_w} c = \frac{57,45}{18} c \quad (18)$$

For $c=0,01$ of ClNa corresponds a value $c' = 3,2 \%$, a value similar to the normal salt concentration in sea-water.

Direct conversion of chemical to mechanical energy is produced in the muscle actions, with relatively high values of thermodynamical efficiencies (20 to 40%).

Artificially mechano-chemical systems have been proposed [11], by means of collagen fiber as a working element and some salt solution as a fuel, producing mechanical work from chemical free energy.

4. Conclusion

The process of chemical energy conversion to mechanical energy without semipermeable membranes above described will require an important experimental and engineering development, but in principle, it will be possible to realize. The use of saline solutions of two different concentrations allows to combine a chemical-mechanical conversion with solar energy, to restore the solution of higher concentration. Moreover, a combination of the energy obtained of the so called "solar ponds" with any of the salinity gradient processes in development could be possible.

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c	v_0 (m/s)	T (° K)	Δt (s)	Δg (J/°Kkg)	Δl (m)	$\frac{\Delta g}{\Delta l}$ (J/°Kkgm)	$\frac{\Delta v^2}{2}$ (m ² /s ²)	ΔH_{\max} (m of water column)	$\Delta H_{1\%}$ (m of water column)
0,005	0,001	293	1	676	1,0	676	0,67	0,069	0,0007
0,01	0,001	293	1	1352	1,0	1352	1,352	0,138	0,0014
0,015	0,001	293	1	2028	1,0	2028	2,028	0,207	0,002
0,005	0,01	293	1	676	1,0	676	6,76	0,69	0,007
0,01	0,01	293	1	1352	1,0	1352	13,52	1,38	0,014
0,015	0,01	293	1	2028	1,0	2028	20,28	2,07	0,02
0,005	0,05	293	1	676	1,0	676	33,8	3,45	0,0034
0,01	0,05	293	1	1352	1,0	1352	67,6	6,9	0,007
0,015	0,05	293	1	2028	1,0	2028	101,4	10,35	0,014

Table 1. ΔH values obtained for some values of the parameters.