Osmosis and Thermodynamics

Uri Lachish, *guma* science
urila@internet-zahav.net

Abstract

van't Hoff formula of osmotic pressure, which is identical to the formula of ideal gas pressure, is a direct outcome of the second law of thermodynamics. The formula is derived by applying a closed cycle reversible and isothermal process that follows an argument in Fermi's book: "Thermodynamics".

Osmosis is the flow of a liquid via a semi-permeable membrane that blocks the passage of particles dissolved within it. The flow direction and rate is controlled by pressure on the liquid solution. For a system where the particles are on a single side of the membrane, the osmotic pressure π, the pressure that stops the flow, is given by van't Hoff's formula (1):

$$\pi = cRT$$

where c is the molar solute concentration, R is the gas constant, and T is the absolute temperature. van't Hoff derived this formula by analogy with the pressure of an ideal gas of the same concentration and temperature. For this hypothesis he received the first Noble prize in chemistry in 1901, but his idea of the analogy was not generally accepted in the years to come. Regarding osmosis, people usually refer to the general theory of thermodynamics and the identity of van't Hoff's formula of osmotic pressure, to the ideal gas pressure, is considered sometimes as surprising or as a coincidence. People also propose

models and mechanisms of solvent pumping by the membrane to account for osmosis. A recent one appears in ref-(2).

Here is a thermodynamic discussion of osmosis that follows Fermi's book "Thermodynamics" (3). Fermi's argument is quoted in Appendix-1.

Consider a vertical cylinder, equipped with an upper and a lower moving piston, divided by a semi-permeable membrane as shown in Figure-1. The cylinder contains a fluid, either a liquid or a gas, or both, that is free to cross the membrane. In addition, there are dissolved particles blocked by the membrane and confined to the cylinder lower volume. It is assumed that there is no chemical interaction between the dissolved particles and the fluid.

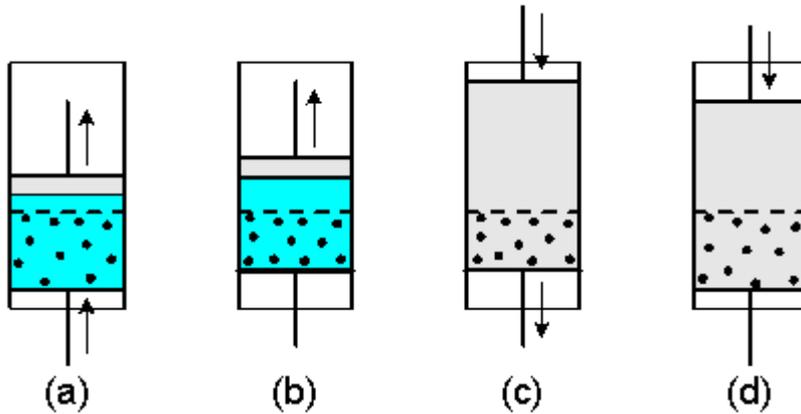Figure-1 describes a cyclic four step reversible process that operates at a constant temperature.

Figure-1: Cyclic isothermal compression and expansion of particles within a fluid. The fluid is free to
          cross the semi-permeable membrane.
          (a)-›(b): Compression of the particles within a liquid (blue). The fluid volume is constant.
          (b)-›(c): Expansion of the fluid to evaporate all the liquid.
          (c)-›(d): Expansion of the confined particles within a gas

(grey). The fluid volume is constant.

    (d)-›(a): Compression of the fluid to partially condense the gas.

    The work of fluid expansion (b) is equal to the work of fluid compression (d). Therefore, by the

    second law of thermodynamics, the work of particle compression within the liquid must be

    equal to the work of particle expansion within the gas.

In step-1 the confined particles in the lower volume are dissolved in a liquid fluid. The two pistons move up together without changing the fluid volume; therefore, there is no work involved with the fluid. However, the lower piston compresses the dissolved particles, between it and the membrane, and does an amount of work $\pi\,dV$ where π is the osmotic pressure. V is the volume of the dissolved particles and dV is a small volume change.

In step-2 the upper piston moves up and induces liquid evaporation of the fluid until it is transformed into a gas. It is assumed that the dissolved particles are now also in a gas phase.

In step-3 the two pistons move down together, again without changing the fluid volume. The confined particles push the lower piston, expand and do a work $p\,dV$ where p is the gas pressure and dV is the same volume change as in step-1.

In step-4 the upper piston moves down, compresses the fluid and induces fluid condensation into a liquid until it arrives at the initial state of the completed cycle.

Since the process is reversible and isothermal the overall work done during the closed cycle must be zero. Otherwise it will violate the second law of thermodynamics as postulated by Kelvin (Fermi, "Thermodynamics", page 30):

"*A transformation whose only final result is to transform into work heat extracted from a source which is at the same*

temperature throughout is impossible."

The work done in step-2, of fluid expansion, is equal to the work done in step-4, of fluid compression, since the two processes are done between the same fluid states. Therefore, the compression work, in step-1, of the confined particles dissolved within a liquid, must be equal to the expansion work, in step-3, of the confined particles in a gas phase. That is, $\pi \, dV = p \, dV$. Therefore, the osmotic pressure of the particles dissolved within the liquid is equal to the ideal gas pressure in the gas phase.

$$\pi = p$$

The identity of van't Hoff's formula of the osmotic pressure to the formula of the ideal gas pressure is, therefore, a direct and fundamental consequence of the second law of thermodynamics.

The argument leading to the equation depends on the assumption that the solute-solvent interaction does not depend on the solute concentration. States (a) and (b) in Figure-1 have different volumes of solvent interacting with the solute so that in non-ideal solutions they are not the same fluid states. As a result the work in step 2 will not be equal to the work in step 4 and the equation will be only approximate.

Osmosis is discussed in textbooks in terms of the free energy G. $\Delta G = 0$, or in terms of the entropy S, $\Delta S = 0$, both for a reversible process. For a reversible closed-cycle and isothermal process:

$$0 = T \, \Delta S = \Delta Q = - \Delta W$$

where ΔQ is the heat transferred to the heat bath, and ΔW is the work done by the system, both in a closed cycle.

Therefore discussions in terms of G, S, or W of a reversible isothermal process are fully equivalent. The discussion of osmosis in terms of W, as presented here, is equivalent to a discussion in

terms of the free energy G.

In Fermi's discussion of osmosis, in terms of the free energy, he applies the entropy of free particles (Fermi, "Thermodynamics", p. 115, equation (153)) which he justifies by considering the system in a vaporized thermodynamic state (see Appendix-1. The idea is followed here). The whole matter is ideal gas in - ideal gas out, so that van't Hoff formula is hardly surprising.

When static pressure is built up within a fluid, Pascal law postulates that the pressure will be distributed equally within the fluid volume and will be perpendicular to the surface of the fluid boundary (gravitation not included). The law is a direct consequence of the conservation law of linear momentum.

Since the dissolved particles are prevented from leaving a volume by a semipermeable membrane they will exert pressure on it (a loose quotation of Einstein (4), see Appendix-2).

Fermi expresses the same idea ("Thermodynamics", page 122, see Appendix-1):

"... Then the pressure on the side of the membrane facing the solution will be increased by the impacts against it of the molecules of the dissolved sub-stances, which cannot pass through the membrane..."

A solute particle exerts pressure by delivering momentum to the membrane. It delivers momentum also to its neighbor molecules, so that the time averaged momentum delivered to the membrane and to the neighbors in all directions is zero, as required by conservation of linear momentum. The non zero momentum delivered to the neighbors, not including the membrane, spreads in all directions toward the solution boundaries and generates pressure on them.

Whenever an osmotic pressure is built-up, according to Pascal law it will act equally on all of the solution boundaries. It will

then push any boundary that is free to move. The osmotic pressure acts on a moving boundary from inside the solution, and in order to keep the system under balance a similar extra external pressure should act on it from outside. If the external pressure is reduced below the osmotic pressure, then solvent will flow via the membrane into the solution, and if the external pressure is increased above the osmotic pressure, then the solvent will flow out of the solution.

These conclusions are direct consequences of fundamental laws. The role of the membrane in osmosis is just to let the solvent go through it and to block the solute. There is no need of microscopic solvent pumping by the membrane.

van't Hoff, in his paper (1), presents a flow scheme in order to verify the osmotic pressure formula. The scheme is not clear and difficult to follow. However, it does consist of a closed cycle that includes an expansion work of particles in a gas phase and a compression work in solution, or vice versa.

van't Hoff also discusses the mechanism of osmosis:

"The mechanism by which, according to our present conceptions, the elastic pressure of gases is produced is essentially the same as that which gives rise to osmotic pressure in solutions. It depends, in the first case, upon the impact of the gas molecules against the wall of the vessel; in the latter, upon the impact of the molecules of the dissolved substance against the semipermeable membrane, since the molecules of the solvent, being present upon both sides of the membrane through which they pass, do not enter into consideration."

van't Hoff original paper on osmosis thus presents a thermodynamic derivation of the osmotic pressure formula and also a rigorous mechanism of osmosis as evidenced by considering Pascal law. A high esteem of van't Hoff work was expressed by Lord Rayleigh (5) (see appendix-3):

"If I suggest a somewhat modified treatment, it is not that I see any unsoundness in van't Hoff's argument, but because of the importance of regarding a matter of this kind from various points of view."

When either solvent molecules or dissolved particles, at liquid boundaries other than the membrane, are prevented from leaving the liquid, they will exert pressure on the boundaries (this remark again follows Einstein (4), see Appendix-2). Therefore, by Neuton's third law, the boundaries exert back the same pressure on the liquid. This pressure, that comes from the molecular attraction forces at the liquid surface, is by far higher than the membrane generated osmotic pressure which is only a small disturbance to it. Therefore the pressure on the liquid is always positive. Contrary to the semi-permeable membrane, at the other boundaries of the pure solvent, or of the solution, there is no difference between solvent and solute collisions with them,

See: The equivalence of van't Hoff's and Rayleigh's arguments with the analysis of chemical potentials.
van't Hoff's Evidence

Appendix-1: THERMODYNAMICS by ENRICO FERMI
Prentic-Hall 1937. Dover Publications, Inc. New York, NY 1956

Chapter VII: The Thermodynamics of Dilute solutions

Page 115:
... "If we now integrate (150), we obtain the expression for the entropy:

$$S = \sum_{i=0}^{g} N_i s_i (T, p) + C(N_0, N_1, ..., N_g)$$
. (152)

The constant of integration C, which is constant only with respect to T and p, depends on the N's; we have put this in evidence in (152). We can determine the value of this constant as follows:

Since no restriction has been placed on the manner in which T and p may vary, the expression (152) for S still applies if we choose p so small and T so large that the entire solution, including all solutes, vaporizes. Our system will then be completely gaseous, and for such a system we already know that the entropy is equal to the sum of the partial entropies of the component gases (see section 23). But the entropy of one mole of a gas at the partial pressure p_i and having the molecular heat C_{pi} is (see equation (87)):

$$C_{pi} \log T - R \log p_i + a_i + R \log R . \qquad (153)$$

Hence, for our mixture of gases we have (since the partial pressure p_i of the substance A_i is equal to $pN_i / (N_0 + \ldots + N_g)$, where p is the total pressure):

$$S = \sum_{i=0}^{g} N_i \left(C_{pi} \log T - R \log p \frac{N_i}{N_0 + \ldots + N_g} + a_i + R \log R \right)$$

$$= \sum_{i=0}^{g} N_i \left(C_{pi} \log T - R \log p + a_i + R \log R \right)$$

$$- R \sum_{i=0}^{g} N_i \log \frac{N_i}{N_0 + \ldots + N_g} .$$

If we compare this with (152), which applies to our gaseous mixture also, we find that:

$$s_i = C_{pi} \log T - R \log p + a_i + R \log R ,$$

and

$$C(N_0, N_1, ..., N_g) = -R \sum_{i=0}^{g} N_i \log \frac{N_i}{N_0 + ... + N_g}$$

.   (154)

But the constant $C(N_0, N_1, ... , N_g)$ *does not depend on*
T or p. Its value (154) therefore applies not only to the
gaseous mixture, but also to the original solution. Hence,
(152) becomes:

$$S = \sum_{i=0}^{g} N_i s_i(T, p) - R \sum_{i=0}^{g} N_i \log \frac{N_i}{N_0 + N_1 + ... + N_g} .$$ *(155)"*

Page 122:
   "The osmotic pressure of a dilute solution is equal to the
pressure exerted by an ideal gas at the same temperature and
occupying the same volume as the solution and containing a
number of moles equal to the number of moles of the solutes
dissolved in the solution.

   This simple thermodynamical result can be easily inter-
preted from the point of view of the kinetic theory. We
consider a container divided into two parts by a semi-
permeable membrane with pure solvent in each part.
Since the solvent can pass freely through the semipermeable
membrane, the pressure on both sides of the membrane will
be the same. Now let us dissolve some substances in one
part and not in the other. Then the pressure on the side
of the membrane facing the solution will be increased by the
impacts against it of the molecules of the dissolved sub-
stances, which cannot pass through the membrane and
which move about with a velocity that depends on T. The

larger the number of molecules dissolved and the higher the
temperature, the larger will be the number of impacts per
unit time and, hence, the greater the osmotic pressure.

It can be shown from the kinetic theory that the velocities of
molecules of the dissolved substances are not affected by
the molecules' being in solution, but are equal to the velocit-
ies that they would have if they were in a gaseous state.
Therefore, both the number and the intensity of the impacts
of the molecules of the dissolved substances against the
membrane are equal to the number and intensity of the
impacts that one expects for a gas. The pressures exerted
in both cases are therefore equal."

Appendix-2*: INVESTIGATIONS ON THE THEORY OF THE*
BROWNIAN MOVEMENT by ALBERT EINSTEIN (4),
Methuen and Co., Ltd., 1927, Dover Publications, Inc. New York,
NY 1956

Page-3:

..."We must assume that the
suspended particles perform an irregular move-
ment – even if a very slow one – in the liquid, on
account of the molecular movement of the liquid ;
if they are prevented from leaving the volume V*
by the partition, they will exert a pressure on the
partition just like molecules in solution."

Appendix-3*: THEORY OF SOLUTIONS - LORD RAYLEIGH (5)*

"As some recent viva voce remarks of mine have received
an interpretation more wide than I intended,
I shall be glad to be allowed to explain that when (now
several years ago) I became acquainted with the work of
van't Hoff I was soon convinced of the great importance
of the advances due to him and his followers. The subject
has been prejudiced by a good deal of careless

phraseology, and this is probably the reason why some distinguished physicists and chemists have refused their adhesion. It must be admitted, further, that the arguments of van't Hoff are often insufficiently set out, and are accordingly difficult to follow. Perhaps this remark applies especially to his treatment of the central theorem, viz. the identification of the osmotic pressure of a dissolved gas with the pressure which would be exercised by the gas alone if it occupied the same total volume in the absence of the solvent. From this follows the formal extension of Avogadro's law to the osmotic pressure of dissolved gases, and thence by a natural hypothesis to the osmotic pressure of other dissolved substances, even although they may not be capable of existing in the gaseous condition. If I suggest a somewhat modified treatment, it is not that I see any unsoundness in van't Hoff's argument, but because of the importance of regarding a matter of this kind from various points of view."

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Links:

1. *Thermodynamics Research Laboratory, http://www.uic.edu/~mansoori/Thermodynamics.Educational.Sites_html*
2. *Thermodynamik - Warmelehre, http://www.schulphysik.de/thermodyn.html*
3. *The Blind Men and the Elephant*
4. *My Spin on Lunacy*
5. *Five Weeks in a Balloon*
6. *The first man I saw*
7. *"Faster, Faster!"*
8. *Perfection can't be rushed*
9. *The man higher up*
10. *Brains*
11. *The First-Class Passenger*

12. [other](#)