

Vapor Pressure Lowering, Osmotic Pressure, and the Elementary Pseudo-Gas Model

Karol J. Mysels*

Chemistry Department, University of California, San Diego, La Jolla, California 92023-0137

Received: August 13, 1996; In Final Form: December 13, 1996[®]

Guided by the apparently mysterious identity of the constant R in the equation describing the pressure of ideal gases (Boyle's law: $P = NRT/V$) and the osmotic pressures of dilute solutions (van't Hoff's law: $\pi = NRT/V$), it is argued that the "pseudo-gas" model is *the* appropriate method for the elementary discussion of dilute solutions. By introducing the concept of "distending pressure" (due to the thermal agitation of the solute molecules), it is shown that this model accounts for the vapor pressure lowering of solutions. Indeed, Raoult's law, now often taken as the basis of discussion, can be derived in the limit of infinite dilution and ideality. The approach also exemplifies how apparently disparate phenomena can be unified on an elementary level.

Introduction

Important support for Newton's theory of gravitation came from the fact that the same constant accounted for both the motion of the earth around the sun and for the motion of the moon around the earth. This was in accord with Ockham's Razor, the principle of keeping the number of hypotheses to a minimum.

On an admittedly less cosmic scale, the identity of the constant R in the laws of gases and of osmotic pressure, as discovered by van't Hoff¹ should have kept his theory in the limelight of the teaching of chemistry. Yet this is clearly not the case.

Some introductory books² do not mention osmotic pressure or colligative properties. Some texts note a "striking"³ or "interesting final result"⁴ but do not discuss its meaning. Others⁵ fail to even note the identity after deriving both Boyle's and van't Hoff's laws. One lengthy article is explicit: "The similarity...is wholly without significance".⁶

In fact, however, elementary molecular–kinetic reasoning invoking only conservation of momentum and equipartition of energy can readily be extended from infinitely dilute gases to infinitely dilute solutions. The resulting "pseudo-gas"⁷ or "tensile solvent"⁸ model provides a unique insight into why colligative properties and especially vapor pressure lowering and osmotic pressure depend solely on the concentration of molecules and not on their size or shape at sufficiently low concentrations.

The neglect of this enlightening and unifying approach, and even antagonism towards it, is disturbing because it affects not only future chemists, who can always fall back on thermodynamics or statistical mechanics to handle dilute solutions, but because it affects especially the practitioners of other disciplines who should know and understand solution properties but are not prepared or willing to tackle the more complicated theories. (Professors please note: that sleepy student in the third row may, in a few years, become the anesthesiologist who puts you to sleep.)

For these nonchemists (and for some chemists too) an easily remembered explanation is in kinetic–molecular terms. Thermodynamics, so valuable in dealing quantitatively with macroscopic effects, is intrinsically unable to operate on the molecular scale. Statistical mechanics offers correct treatment but certainly with a much higher degree of difficulty.

The present paper aims at convincing the reader that the pseudo-gas model is *the* correct elementary explanation and can enrich any elementary presentation of chemical theories.

Pseudo-Gas Model. Briefly stated, the pseudo-gas view is that in many respects the solvent acts like the container of a gas and the solute, driven by thermal agitation, exerts a distending pressure upon the solvent like a gas would on the container. It is this distending pressure that lowers the activity (i.e., the vapor pressure) of the solvent and is equal and opposite to the osmotic pressure. Quite different explanations are generally presented and we examine briefly their weaknesses.

Popular but Wanting

Impeded Evaporation. A common explanation starts with the kinetic–molecular picture of liquid–vapor equilibrium due to equal rates of condensation and evaporation at the surface. It then postulates that the solute molecules obstruct the evaporation from the surface (but not the condensation on it) thus leading to a new and lower equilibrium vapor pressure (i.e., a lower activity of the solvent).

This theory was introduced by T. Martin Lowry at the second "General Discussion" of the Faraday Society in 1907.^{9,10} It was criticized already by Findlay^{11,12} for its disregard of the effect of surface concentration changes due to adsorption. To state it otherwise: activity or vapor pressure are bulk properties and cannot depend on a surface process.

An independent objection¹³ is that this picture does not conform to the principle of microscopic reversibility: evaporation and condensation proceed by different paths. Hence, a catalyst for one path would shift the equilibrium and permit perpetual motion.

Lowry later became Professor of Physical Chemistry at Cambridge and this may have contributed to the spread of his theory and its inclusion in many textbooks. Criticism in a Textbook Errors column¹³ 40 years ago seems to have removed "impeded evaporation" for a time from such books but recently it has reappeared in some, as well as in a recent Provocative Opinion column.¹⁴

Solvent Dilution. This explanation has been very clearly stated by F. C. Andrews: "The solute simply lowers the concentration of solvent in the solution as compared to the pure solvent. The colligative properties follow directly from this dilution of the solvent by solute".¹⁵

This sounds simple and convincing, but what happens when we compare solute molecules of very different sizes, say methane and C-870 fullerene? Clearly each molecule of the latter dilutes the solvent more than a molecule of the former,

* Author to whom all correspondence should be addressed: 8327 La Jolla Scenic Dr., La Jolla, CA 92037; (619) 453-6988.

[®] Abstract published in *Advance ACS Abstracts*, February 15, 1997.

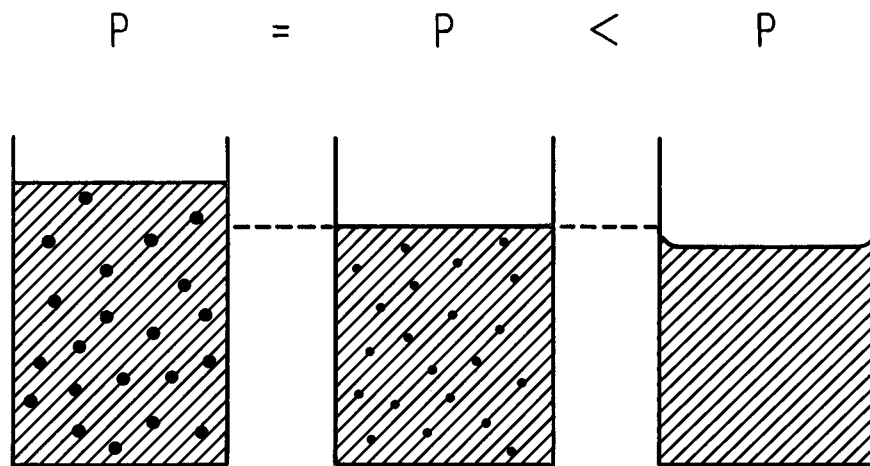


Figure 1. Equal numbers of molecules of differing volumes dissolved in the same volume of a solvent generally give different volumes of solution. It is difficult to simply explain why their vapor pressure lowering should be the same without considering equipartition of energy (see text).

yet, in the limit of infinite dilution they must produce the same vapor pressure lowering; hence, the same change in activity. Thus this explanation is also unsatisfactory.

If one compensates for the size differences by using mole fractions, then the equal effect on vapor pressure no longer “follows directly”.

Consider Figure 1 showing three beakers each containing the same amount of solvent and the first and second also the same number of solute molecules, but these molecules are large in the first beaker and small in the second one. In general we obtain very different volumes of solution in each beaker, yet we have to explain that the vapor pressure is the same in the first two and higher in the third one. This seems very difficult without introducing some quantity common to all solutes such as equipartitioned energy. This will be done below.

The same argument against the solvent–dilution theory can be made on the basis of the effect of solvation of the solute. This certainly changes the dilution of the solvent but not its activity. Yet another argument will be presented later at the end of the Osmotic Pressure section.

Diffusivity. Explanations of osmotic pressure have been based on diffusivity: “the tendency of any gas to fill its container and of any solute to diffuse throughout the solvent accessible to it”.¹⁶

Two points may be raised against this basically sound approach. One is that it is not a kinetic molecular explanation but a macroscopic one. It is only one step short of recognizing thermal agitation as the primary cause of the “diffusivity”, but this step is left in limbo. The second point is that the rate of diffusion depends on the size and shape of the molecules and the student might erroneously assume that osmotic equilibrium does as well.

Pseudo-Gas Model

Liquid and Gas. Liquids are of course very different from gases, and it may not be obvious that the laws of gases apply to solutes. Molecules of a liquid spend most of their time in collisions, and their free path is incomparably shorter than in the gas.

The effect of length of collision time may be accounted for by including the potential energy with the kinetic one or it can be sidestepped by using a “hard sphere” model which reduces this time to zero. Thus equipartition of equivalent energy can be expected to hold. Given equal molecular weights, this leads also to equal velocities.

In the long run, due to their thermal agitation, molecules of a gas, as well as those of a solute, occupy all positions of their space. As they have the same velocities, they undergo the same

number of collisions with the wall and it is plausible that they exert the same pressure on their boundaries. The identity of the two R constants follows directly.

Incidentally, even solid solutions lead to the same statistical thermodynamic equations despite the “no resemblance” of models.¹⁷

To support these statements, let us examine qualitatively but in more detail what the molecules are doing in a solution.

Simplest Model. Consider a sample of a nonvolatile liquid solvent in a vacuum and at zero gravity, and let us place a small quantity of a nonvolatile solute in it. If intermolecular forces are within the proper limits, thermal agitation causes dissolution and the solute will tend to distribute itself uniformly throughout the solvent, diffusing, as would a gas, by the random motion of its molecules.

At the boundary, the spread of the solute is stopped, like the spread of a gas is stopped by the containing vessel. In either case, the average momentum of the reflected molecules is reversed at the boundary. The gas thus exerts its pressure on the vessel, and in our case the solute exerts its distending pressure onto the confining solvent. This dilates the solvent till this distending pressure is balanced by the cohesive forces of the solvent. (If zero pressure is taken as that of the pure solvent, the distending pressure must carry a negative sign, i.e., it must be a tension.)

It may be noted that this argument involves the boundaries of the solution but does not depend on their equilibrium composition or properties. It is the stream of molecules reflected back at all boundaries that produce the distending pressure. Though the distending pressure is generated at the boundaries, it is transmitted to the whole liquid as is all hydrostatic pressure.

As is well-known, pressure affects the escaping tendency (i.e., the activity of a system). Increasing the outside pressure raises the activity (vapor pressure), whereas decreasing this pressure lowers the activity (vapor pressure). Distending pressure has the opposite effect.

Thus in our case the distending pressure produced by the thermal agitation of the solute lowers the activity of the solvent. The liquid solvent has less tendency to “spit out” its molecules and more tendency to “suck them in” from the vapor.

Implied in this argument is the neglect of any effect of the solute upon the solvent, except for the distending pressure. This is justified at infinite dilution where all effects decaying with distance disappear, and only those, such as hydrostatic pressure, which do not decrease with distance, persist.

Solution in a Semipermeable Vessel. Let us consider the effect of placing our solution in a gravitational field in a

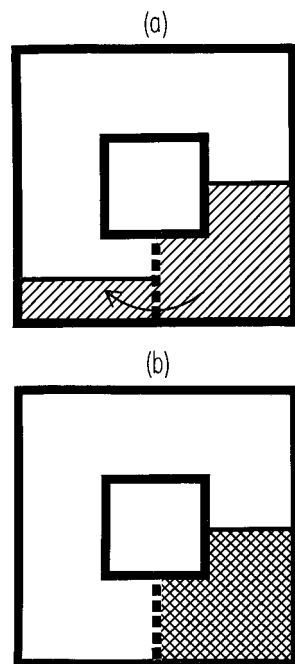


Figure 2. (a) A semipermeable membrane permits the flow of pure solvent (hatched) under minor pressure gradients. (b) The same membrane prevents the flow of solvent from a solution (crosshatched) unless a pressure exceeding the osmotic pressure is applied to the solution.

semipermeable vessel, open to the solvent but closed to the solute. The pure solvent will leak out across the walls of the vessel by gravity. Yet a sufficiently concentrated solution will be retained, as indicated in Figure 2. In the latter case, the solvent is not retained directly by the membrane (since pure solvent passes freely under the same conditions). It is pulled into the interior and held there by the distending pressure of the solute. In other words, for the solvent to cross the semipermeable membrane, the distending pressure of the expansionist solute has to be overcome.

Thus the membrane remains dry on the outside until a sufficient pressure ($\pi \geq NRT/V$) is applied on the solution inside the vessel. Only then is pure solvent forced out of the vessel. (This is the basis of the "reverse osmosis" method of water purification.)

Osmotic Pressure

The most interesting case, of course, is when solvent is brought in contact through a semipermeable vessel with an enclosed solution. Now the solvent can move not only out of the vessel but also into it either by thermal agitation or by a hydrostatic pressure differential.

The system can be brought to equilibrium, as indicated in Figure 3, either by increasing the hydrostatic pressure on the solution side or by applying an equal negative pressure on the solvent side, thus balancing out the effect of thermal agitation of the confined solute molecules. The pressure difference prevailing at equilibrium is, of course, the equilibrium osmotic pressure or, briefly, the osmotic pressure. As found by van't Hoff¹ more than a century ago, it is given by $\pi = NRT/V$ in agreement with the pseudo-gas model as well as simple thermodynamics.

The lack of dependence on solvent properties means that the osmotic pressure is independent of the volume of the solvent molecules or of their interactions. In particular, if a solvent polymerizes or "associates", as water does upon condensation, there is no effect on osmotic pressure. This is difficult to reconcile with the "solvent dilution" explanation.

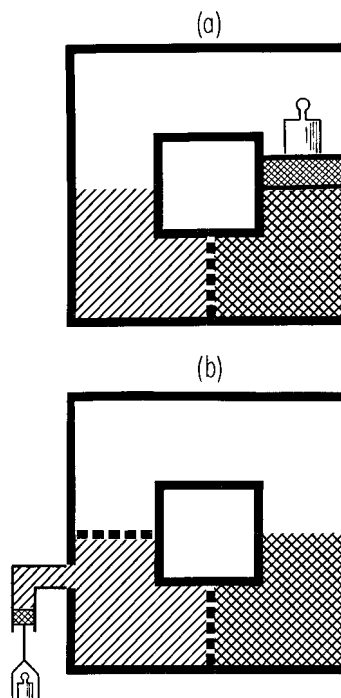


Figure 3. Osmotic equilibrium may be achieved either by applying positive pressure to the solution or negative pressure (tension) to the solvent.

Raoult's Law

The advantage of using or teaching the pseudo-gas model would be considerably reduced if Raoult's law required an independent or higher level derivation. The following simple argument, which I have not encountered in the literature, shows how the pseudo-gas model leads directly to Raoult's law which requires not only that the fractional vapor pressure lowering $(P_0 - P)/P_0$ be proportional but that it be equal to the mole fraction X of the solvent. More simply, $P/P_0 = X$ at least in the limit of infinite dilution.

Let us consider a group of dilute solutions of different solutes but of the same mole fraction and all in the same solvent. According to our model they all have the same distending pressure. As this pressure acts on the same almost pure solvent, it produces the same vapor pressure lowering in each of these solutions. Thus we need to know only how one solute affects this solvent to know how all other solutes affect it.

The natural source for obtaining this information is a solution so ideal it is one in which the solvent is chemically so close to the solute as to have practically the same vapor pressure. Such similarity of molecules leads to a corresponding similarity of distribution between the two phases (i.e., the mole fraction becomes the same in liquid and vapor in the limit of dilution and ideality). Such an ideal solution thus obeys Raoult's law. Hence, all solutions in the chosen solvent obey it too. As we have placed no limitation on the choice of this solvent, Raoult's law must apply also to all solvents.

Conclusion

Ockham's Razor clearly points the way: the elementary pseudo-gas model provides a simple but correct and unifying approach to explaining vapor pressure lowering and osmotic pressure. It leads to the same results as statistical mechanics,^{18,19} or a more detailed view of collisions.^{20,21}

There are many more peripheral points that have been raised since van't Hoff's time. I will consider some of them as a series of asides (i–iv).

i. Negative Pressure. Chinard probably expressed the view of many people when he wrote: "...There is no justification or

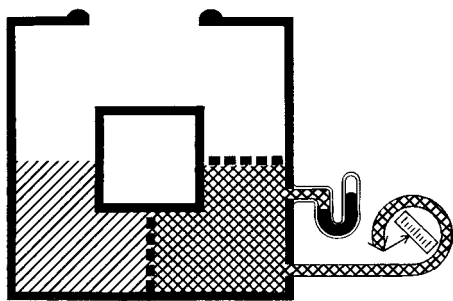


Figure 4. If the solute is volatile, osmotic equilibrium requires that it be separated completely from the solvent by impervious or semipermeable walls. In the absence of a free surface, osmotic pressure can be measured by a Bourdon gauge or a mercury manometer.

basis for the concept of negative pressure: pressure approaches zero as the molecular density approaches zero, but pressure does not and cannot assume negative values".²²

This is true for gases, but in fact, mercury often sticks to the closed end of the barometric tube, and thus is under tension (i.e., negative pressure), until tapping lets it fall.

More quantitatively, for water and other liquids the rupture under tensions of more than a 100 atm has been studied since Berthelot's 1850 experiments.²³ Perhaps the most convincing are the results of Briggs.²⁴

If one remembers that molecules of a liquid attract each other strongly and are thus under large internal pressures²⁵ (or have a high cohesive energy density), it is easy to see that a minor disturbance in these interactions produced by osmotic effects in dilute solutions can be easily accommodated without major upheaval.

We should also note that if our thought experiments involving distending pressures included an added inert and insoluble gas at sufficiently high pressure, none of the tensions discussed would generate negative pressures, therefore, the latter have really no bearing on the main argument. However, negative pressures become important when considering such real life problems as the rise of sap in trees^{8,26} or cavitation.²⁷

The peripheral role of negative pressure and tension in the explanation of activity lowering makes "pseudo-gas" a much more appropriate name for this model than the "tensile solvent" name sometimes used for it.^{8,28}

ii. Membrane. Obviously, all truly semipermeable membranes must give the same osmotic pressure for the same solution-solvent system or else perpetual motion would be possible. Thus the details of what makes a membrane semipermeable in a particular system can have no bearing on the value of the osmotic pressure. They may, however, be crucial for the kinetics involved.

Osmotic thought experiments are generally depicted with a free surface at which the osmotic pressure originates.^{8,21} This is not essential, as shown in Figure 4. However, a semipermeable membrane and a deformable boundary are essential for this mechanical manifestation of activity lowering.

iii. Volatile Solute. Frequently, in an osmotic thought experiment, the solution and the solvent, though separated by a membrane, are shown communicating through the vapor space. This presents no problem if the solute is nonvolatile; when the solute is volatile, the free surface in conjunction with the vapor space provides a bypass of the semipermeable membrane. Hence, to produce an equilibrium osmotic system with a volatile solute, the solution compartment must be closed by impervious or semipermeable walls. Of course, the osmotic pressure can still be measured by a mercury manometer or a Bourdon gauge (a spiral tubing which tends to straighten by internal pressure), as indicated in Figure 4.

Volatility of the solute also introduces a complication into the argument for the pseudo-gas model because now there is a partial flux of solute molecules reaching the free surface which do not reverse course (and momentum) but continue into the gas phase. However, at equilibrium, there must be an equal and opposite flux of solute gas molecules condensing on that same free surface of the solution (and bringing in their momentum). These two fluxes neutralize each other exactly and the distending pressure is not affected by this volatility.

iv. Are All Pressures Osmotic? MacMillan and Mayer¹⁸ point out that "all pressures would be osmotic" in a hypothetical system comprising "intangible molecules which act with forces on the ordinary molecules but which could pass through them. Their fugacity could be everywhere constant though not their concentration".

A steel gas cylinder would then fully satisfy the definition of a semipermeable vessel for, say, nitrogen as the solute and the intangible particles as the solvent. There would be no question that the osmotic pressure is exerted by the solute (the nitrogen) upon the semipermeable membrane (the cylinder).

To round out this picture, we would need a second type of hypothetical molecules capable of forming a completely impervious wall to enclose the whole system so that it can reach equilibrium.

Acknowledgment. I thank G. S. Hartley, P. Mukerjee, E. K. Mysels, L. Nash, J. Th.G. Overbeek, M. Troll, A. Vrij, J. Wheeler, and B. Zimm for helpful critical discussions and suggestions of important references.

References and Notes

- (1) van't Hoff, J. *Z. Phys. Chem. (Munich)* **1887**, *1*, 481–506. *Foundations of the Theory of Dilute Solutions*; Alembic Club Reprints 19; Livingstone: Edinburgh, 1961.
- (2) Pimentel, G. C.; Spratley, D. S. *Understanding Chemistry*; Holden-Day: San Francisco, 1971.
- (3) Adamson, A. W. *A Textbook of Physical Chemistry*; Academic Press: New York, 1973.
- (4) Pauling, L. *College Chemistry; an Introductory Textbook of General Chemistry* Freeman: San Francisco, 1964. Pauling, L. *General Chemistry*; Dover: New York, 1988.
- (5) Eggers, D. F., Jr.; Gregory, N. W.; Halsey, G. D., Jr.; Rabinovitch, B. S. *Physical Chemistry*; Wiley: New York, 1964.
- (6) Babcock, K. L. *Hilgardia* **1963**, *34*, 417–542 (p 435).
- (7) Hildebrand, J. H. *Science* **1955**, *121*, 116–119.
- (8) Hammel, H. T.; Scholander, P. F. *Osmosis and Tensile Solvent*; Springer: Berlin, 1976.
- (9) Lowry, T. M. *Trans. Faraday Soc.* **1907**, *3*, 14–21.
- (10) Lowry, T. M. *Philos. Mag.* **1907**, *13*, 552–559.
- (11) Findlay, A. *Trans. Faraday Soc.* **1907**, *3*, 31–34.
- (12) Findlay, A. *Osmotic Pressure*; Longmans, Green and Co.: London, 1919.
- (13) Mysels, K. J. *J. Chem. Educ.* **1955**, *32*, 179.
- (14) Hawkes, S. J. *J. Chem. Educ.* **1995**, *72*, 204–5.
- (15) Andrews, F. C. *Science* **1976**, *194*, 567–571.
- (16) Lewis, G. N.; Randall, M. *Thermodynamics*, 2nd ed.; Pitzer, K. S.; Brewer, L., Eds.; McGraw-Hill: New York, 1961.
- (17) Gurney, R. W. *Introduction to Statistical Mechanics*; McGraw-Hill: New York, 1949.
- (18) McMillan, W. G.; Mayer, J. E. *J. Chem. Phys.* **1945**, *13*, 276–305.
- (19) Ehrenfest, P. *Proc. K. Ned. Akad. Wet.* **1915**, *17* (2), 1241–1243.
- (20) Oster, G.; Peskin, C. S. *Swelling Mechanics: From Clays to Living Cells and Tissues*; Karalis, T. K., Ed.; Springer: New York, 1992.
- (21) Lachish, U. L. *J. Chem. Educ.* **1978**, *55*, 369–371.
- (22) Chinard, F. P.; Enns, T. *Science* **1956**, *124*, 472–474.
- (23) Berthelot, M. *C. R. Seances Acad. Sci., Ser. Mec., Phys., Chim., Astron.* **1850**, *30*, 819–821.
- (24) Briggs, L. *J. Chem. Phys.* **1951**, *19*, 970–972.
- (25) Barton, A. F. M. *J. Chem. Educ.* **1971**, *48*, 156–162.
- (26) Bonner, J. *Science* **1959**, *129*, 447–450.
- (27) Knapp, R. T.; Daily, J. W.; Hammit, F. G. *Cavitation*; McGraw-Hill: New York, 1970.
- (28) Mysels, K. J. *J. Chem. Educ.* **1978**, *55*, 21–22.