



A new approach to derivation of Van't Hoff equation for osmotic pressure of a dilute solution

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Abstract: Relative lowering of vapour pressure which is a colligative property of dilute solution of non volatile solute in a volatile solvent has been determined theoretically by applying conditions of Raoult's law. Other colligative properties also have theoretical basis but osmotic pressure which is also a colligative property is expressed by an equation which was deduced empirically by Van't Hoff. Van't Hoff's theory of dilute solutions supports the view that solute particles in a dilute solution behave in a manner similar to that of gas molecules in a gas i.e solute molecules obey Boyle's law, Charles law and Avogadro's law. In this paper it is suggested that it is not the solute molecules but volatile solvent molecules present in a dilute solution that behave like gas molecules in a gas. Here an attempt is made to derive Van't Hoff equation by applying Raoult's law and by considering the pressure exerted by molecules of the solvent in liquid state on the basis of proposed "theory of solvent pressure".

I. Introduction

In case of ideal gases Boyle's law, Charles law and Avogadro's law are followed and ideal gas equation $PV = nRT$ is obeyed[1]. In analogy with gases, dilute solutions are also found to obey similar equation concerning variation of osmotic pressure with concentration of solute. Osmosis has been explained in literature and osmotic pressure of dilute solutions which is a colligative property, is expressed by Van't Hoff equation $\pi = CRT$, which is similar to ideal gas equation[2]. The analogy between dilute solutions and gases may be explained by considering the volatile component of a dilute solution i.e the solvent molecules as a peculiar condition of a gas in which the intermolecular distance and intermolecular forces are such that it comes under the definition of a liquid. As molecules in a gas are continuously colliding with the walls of container, pressure is exerted by a gas. This pressure is determined on the basis of kinetic molecular theory of gases. Solids cannot exert such pressure as the molecules are not free to impart collisions. Liquid state is in between the gaseous state and solid state and molecules in a liquid move under the influence of intermediate intermolecular forces. Van der Waals equation was proposed for real gases considering the existence of intermolecular force of attraction among molecules. In this equation pressure correction term was added to take into account the intermolecular forces. If liquid is considered to be condensed gas, a pressure correction term may be added to pressure in ideal gas equation to express pressure exerted by liquid molecules also. The proposed "theory of solvent pressure" is based on the concept that in spite of the fact that unlike gases, a volatile liquid is not affected by external pressure it has its own pressure just like gases due to mobility of molecules. It is obvious that as liquid forms vapours which contribute to vapour pressure of a liquid, an equal and opposite pressure is exerted by the liquid to be in equilibrium. Liquid has molecules moving continuously and hence have kinetic energy. Velocity distribution among the molecules is such that fraction of molecules having highest value of velocity or lowest value of velocity is very less whereas a large fraction of molecules possess an average velocity. Molecules with high velocity leave the surface of liquid and form vapour. The pressure exerted by the solvent molecules of a volatile liquid is different from the pressure exerted by the molecules of the same liquid present in gaseous state because liquid molecule is under the influence of neighbouring molecules which attract it. Due to this intermolecular force of attraction operating in a liquid which occupies a volume V at temperature T , actual pressure exerted by n moles of a volatile solvent is expressed by adding a correction term to the pressure exerted by gaseous molecules i.e. $(nRT/V) + p'$

According to the proposed "theory of solvent pressure", when a volatile liquid is present in a container, the molecules with sufficient kinetic energy to leave the liquid as vapour create a pressure at the boundary. This pressure is related to the pressure exerted by the solvent molecules if they were present in vapour state. The movement of liquid molecule is restricted by the surrounding liquid molecules which attract it in opposite direction. Hence effective pressure exerted on a barrier is obtained by adding a correction term to the pressure that the liquid would have exerted had it been present in vapour state occupying the same volume as the liquid

occupied. Such is the condition when a solvent and a dilute solution are placed in a container in which a semipermeable membrane separates the two liquids. The osmotic pressure created is equal to the difference of pressure on the two sides of the semipermeable membrane. Osmotic pressure is expressed by Van't Hoff equation which can be deduced theoretically on thermodynamic basis. Some researchers have proposed new equation to replace Van't Hoff osmotic pressure equation [3] and some others have proposed significantly different view of the traditional theory of osmosis [4] but the proposed "theory of solvent pressure" supports and justifies Van't Hoff equation.

II. Derivation of equation for pressure exerted by volatile component of a dilute solution

The pressure developed at dilute solution is due to solvent molecules only as they form the volatile component of the solution. As vapour state is same as gaseous state, vapour which follows Boyle's law, Charles's law and Avogadro's law, exerts a pressure on liquid given by,

$$P = nRT/V$$

where P is pressure of vapour,

V is volume of vapour,

n is the number of moles of vapour,

R is gas constant

T is absolute temperature.

When liquid is considered to be in the form of vapour having same number of moles n and occupying the same volume V at temperature T, it obeys gas laws and the pressure exerted by it is equal to nRT/V .

Molecules of a volatile solvent are supposed to be exerting a pressure on semipermeable membrane if they contain n number of solvent molecules present in V volume at temperature T. But the pressure exerted by a liquid is different from the pressure exerted by the vapours of the same liquid occupying the same volume as that of liquid, as there is intermolecular force of attraction operating among the molecules. Each molecule is being attracted by surrounding molecules so that net pressure exerted by solvent molecules is equal to $nRT/V + p'$ where p' is the pressure correction term. Pure solvent and dilute solution both exert pressure due to the presence of volatile solvent molecules. Pressure exerted by solvent molecules in a dilute solution is equal to $X_A (nRT/V) + p'$ where X_A is the mole fraction of solvent molecules.

III. Derivation of Van't Hoff equation by applying the theory of solvent pressure and Raoult's law

Considering a solvent and a dilute solution separated by a semipermeable membrane, the pressure exerted by pure solvent on semipermeable membrane = $n_A RT/V_1 + p'$

Where n_A = number of moles of solvent molecules in liquid state,

And V_1 is volume of solvent.

R = gas constant

T = absolute temperature

P' = pressure correction term

As there is dilute solution of same solvent on the other side of semipermeable membrane, pressure exerted by dilute solution on semipermeable membrane is given by,

$$= P_A^0 X_A + p'$$

Where P_A^0 = pressure of pure solvent if present in gaseous state occupying same volume as that of liquid.

X_A = the mole fraction of solvent

Pressure exerted by dilute solution

$$= P_A^0 (1 - X_B) + p'$$

Where X_B is mole fraction of nonvolatile solute in the solution

The difference in pressure at the two sides of the semipermeable membrane,

$$= P_A^0 + p' - (P_A^0 X_A + p')$$

$$= P_A^0 - P_A^0 (1 - X_B)$$

$$= P_A^0 X_B$$

Replacing P_A^0 by $n_A RT/V_1$

difference in pressure = $(n_A RT/V_1) X_B$

But $X_B = n_B/(n_A + n_B)$

where n_B is the number of moles of solute in the dilute solution.

Osmotic pressure = $(n_A RT/V_1) \cdot \{n_B/(n_A + n_B)\}$

As in dilute solution, $n_B \ll n_A$, n_B in the denominator can be ignored.

Hence osmotic pressure = $(n_A RT/V_1) \cdot \{n_B/n_A\}$

$$\pi = n_B RT/V_1$$

or

$$\pi = CRT$$

where C is the molar concentration of solute in the solution.

IV. Derivation of expression for osmotic pressure in case of dilute solutions of different concentrations separated by semipermeable membrane

Equation for osmotic pressure developed in case of equal volume of two solutions having different concentrations of same solute on the two sides of the semipermeable membrane:

$$\Pi = P_{A1} - P_{A2}$$

Where Π is the osmotic pressure developed,

P_{A1} is the pressure on one side of the semipermeable membrane due to solution having lower concentration of solute (n_{B1}/V_1)

P_{A2} is the pressure on the other side of the semipermeable membrane due to solution having higher concentration of solute (n_{B2}/V_1),

Applying Raoult's law, difference in pressure developed on the two sides of the membrane

$$= P_A^0 X_{A1} + p' - (P_A^0 X_{A2} + p')$$

Where X_{A1} is the mole fraction of solute in the solution which is more dilute and X_{A2} is the mole fraction of solute in the solution which is less dilute.

Replacing P_A^0 by $n_A RT/V_1$ osmotic pressure

$$= (n_A RT/V_1) [X_{A1} - X_{A2}]$$

$$= (n_A RT/V_1) [1 - X_{B1} - (1 - X_{B2})]$$

$$= (n_A RT/V_1) [X_{B2} - X_{B1}]$$

$$= (n_A RT/V_1) \left[\frac{n_{B2}}{n_A + n_{B2}} - \frac{n_{B1}}{n_A + n_{B1}} \right]$$

As $n_{B1} \ll n_A$ and $n_{B2} \ll n_A$, neglecting n_{B1} and n_{B2} in the denominator, osmotic pressure is expressed as,

$$\Pi = (n_A RT/V_1) \{n_{B2} - n_{B1}\}/n_A$$

$$= (n_{B2} - n_{B1}) RT/V_1$$

$$= [(n_{B2}/V_1) - (n_{B1}/V_1)] RT$$

$$= (C_2 - C_1) RT$$

where C_1 and C_2 are the molar concentrations of the two solutions.

V. Conclusion

It is possible to deduce Van't Hoff equation for osmotic pressure of dilute solutions on the basis of proposed "theory of solvent pressure". In case of dilute solutions which obey Raoult's law, newly proposed theory of solvent pressure provides a better understanding towards the fact that molar amount of solute particles appears in the Van't Hoff equation whereas osmotic pressure is a property that results in the flow of only solvent molecules across the semipermeable membrane. According to Van't Hoff's theory of dilute solutions, osmotic pressure is regarded as the pressure exerted by solute molecules if they were present in gaseous state occupying the same volume as that of solution. In the present paper it is suggested that volatile solvent molecules in a dilute solution behave like gas molecules in a gas, pressure exerted by them being expressed as the sum of pressure exerted by an ideal gas and a pressure correction term. On the basis of Proposed theory of solvent pressure it can be made clear that it is the volatile component of solution i.e the solvent that has its own pressure even in liquid state and it is while deducing expression for osmotic pressure that molar amount of non volatile solute appears in the Van't Hoff equation reflecting that osmotic pressure is a colligative property.

References

- [1] Samuel Glasstone, "Textbook of Physical Chemistry", second edition, 1946.
- [2] J.H. Van't Hoff, "The role of osmotic pressure in the analogy between solutions and gases", Zeitschrift fur physikalische Chemie 1, (1887) 481-508.
- [3] Hung-Chung Huang, Rongging Xie, "New osmosis law and theory: The new formula that replaces Van't Hoff osmotic pressure equation", arxiv.org.
- [4] Larry D. Howlett, "The theory of osmosis", ASME 2003 International Mechanical Engineering Congress and Exposition, (2003) 249-262.