New Osmosis Law and Theory: the New Formula that Replaces van’t Hoff Osmotic Pressure Equation

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Preamble

van't Hoff, a world-renowned scientist, studied and worked on the osmotic pressure and chemical dynamics research to win the first Nobel Prize in Chemistry. For more than a century, his osmotic pressure formula has been written in the physical chemistry textbooks around the world and has been generally considered to be "impeccable" classical theory. But after years of research authors found that van’t Hoff osmotic pressure formula cannot correctly and perfectly explain the osmosis process. Because of this, the authors abstract a new concept for the osmotic force and osmotic law, and theoretically derived an equation of a curve to describe the osmotic pressure formula. The data curve from this formula is consistent with and matches the empirical figure plotted linearly based on large amounts of experimental values. This new formula (equation for a curved relationship) can overcome the drawback and incompleteness of the traditional osmotic pressure formula that can only describe a straight-line relationship.
Abstract
This article derived a new abstract concept from the osmotic process and concluded it via "osmotic force" with a new law -- "osmotic law". The "osmotic law" describes that, in an osmotic system, osmolyte moves osmotically from the side with higher "osmotic force" to the side with lower "osmotic force". In addition, it was proved mathematically that the osmotic process could be explained perfectly via "osmotic force" and "osmotic laws", which can prevent the difficulties in using current "osmotic pressure" concept to explain the osmotic process and phenomenon. A theory and equation to describe the curve of osmotic pressure vs. different ideal solution concentrations are also derived, which can overcome the limitedness and incompleteness of van't Hoff osmotic pressure formula (a linear equation) which is applicable to ideal dilute solution only.

Keywords: osmotic pressure; osmotic force; semipermeable membrane; osmotic effective area; osmotic law.

1. Osmotic Force
The van't Hoff theory describes that substances in dilute solution obey the ideal gas laws, resulting to the osmotic pressure formula \( \pi = (n/V)RT = [C_i]RT \) where \( R \) is the gas constant, \( T \) the absolute temperature, and \( [C_i] \) the molar concentration of solute \( i \) in dilute solution \((1)\). Although people used "osmotic pressure" to explain osmotic process, it often appears to be in conflict or contradiction situation \((2)\) and doesn't make sense even after all kinds of interpretations via pressure \((3)\). The reason for this is, objectively, there must be another concept (not abstractly derived yet until in this article) that can explain the osmotic process clearly and substantially. The authors believe the "osmotic force" should be the new concept to consider.

1.1 The Concept of Osmotic Force
Osmotic force is the force caused by osmotic substance via contact pressure on "semipermeable membrane" (abbreviated "membrane" in this article); its value equals to the pressure strength on the membrane times the osmotic effective area.
The so-called "osmotic force" caused via substance contact pressure on semipermeable membrane comes from the pressure via the contact of osmotic substance (e.g., the solvent water) on the membrane.

The so-called "pressure strength on the membrane" consists of not only the liquid pressure on the membrane, but also including the atmospheric pressure. Although the atmospheric pressures are the same on the two sides of the membrane, there are differences in the liquid pressures (caused by different solution concentrations on the two sides of the membrane in Figure 1A) and the osmotic forces enhanced by the same atmospheric pressure on the two sides are different (Figure 1A). This can be described as the "different effects with same amounts" caused by the "same" atmospheric pressure on the two sides of membrane; the more the liquid concentration difference is, the higher the different effects would be. This is one reason that would interfere with the accuracy of the van't Hoff law; it's also another reason the osmotic pressure found in the plant body in some textbooks is such high to surprise people. Therefore, the equal amounts of atmospheric pressures on the two sides of the membrane cannot be ignored, or "cancelled out".

The so-called "osmotic effective area" is the area contacted by the osmotic substances. Although osmotic substances and non-osmotic substances contact and occupy the membrane area altogether, only the area contacted and occupied by the osmotic substances is effective for the process of osmosis (other area can be called "osmotic ineffective membrane area"). Although the exact positions of the effective and ineffective areas change instantaneously, the ratio between them is constant and fixed in a solution with same concentration. The absolute values for these two kinds of membrane areas are not easy to be measured, but the effective and ineffective membrane areas on the solution side (right side of the tubing in Figure 1) can be derived and calculated via the equal osmotic forces on the two sides of the membrane in osmotic equilibrium (Figure 1C) and that 100% membrane area of the pure water side (left side of the tubing in Figure 1) should be osmotic effective. This kind of derivation and calculation has its unique merit; because it's based on the exact measurement, it can resolve the bias and unfit limit of van't Hoff law on some solutions, e.g., linear and soft macromolecular solution, hydrophilic colloidal solution, electrolyte solution, high concentration solution, …etc.
1.2 Related Formulas Derived from Osmotic Force

After understanding the concept of "osmotic force", we can subsequently derive a series of related formulas (for osmotic law) as shown below:

(1) Formula for "osmotic force": \( F = PS' \) or \( F = PS(1-[Ci]k) \) where \( F \) is "osmotic force"; \( P \) is the pressure on the membrane; \( S' \) is the osmotic effective membrane area; \( S \) is membrane total area; \([Ci]\) is the molar concentration of the solute \( i \) in solution; \( k \) is the equilibrium constant, being the fraction of the ineffective membrane area (over total membrane area) which is contributed by the unit molar concentration of the ideal solution. Thus, \((1-[Ci]k)\) is known to be the fraction of osmotic effective membrane area (over the total membrane area). Note that the real ideal solution doesn't exist and the solution was just idealized for the research purposes. Thus the \( k \) constant for the ineffective membrane fraction per unit molar concentration in ideal solution is hard to measure; in the real application in the real world, the \( k \) values may vary in different kinds of solutions. Nonetheless, this won't affect our understanding in theory that there is a standard and constant \( k \) value in ideal solution, which can facilitate the setup of a unified mathematical model or formula for the further and deeper understanding of the solution's property and characteristic features.

(2) Formula for "net osmotic force": \( \Delta F = PaS'a - PbS'b \) where \((Pa, S'a)\) and \((Pb, S'b)\) are the pressure strength and the osmotic effective membrane area on the two sides of the membrane respectively. If \( \Delta F > 0 \), the net osmosis process is going on from \( a \) side to \( b \) side; if \( \Delta F < 0 \), the net osmosis process is going on from \( b \) side to \( a \) side.

(3) Formula for "osmotic equilibrium": \( PaS'a = PbS'b \), i.e., \( \Delta F = 0 \), osmosis is at the status of "dynamic equilibrium".

(4) Formula for "osmotic effective membrane area": \( S' = SPw/Ps \) where \( Pw \) and \( Ps \) are the pressure strength in the (pure) water side and solution side respectively during osmotic equilibrium (Figure 1C).

(5) Relational Formula for the "membrane areas": \( S = S' + S'' \) where \( S' \) and \( S'' \) are the osmotic effective and ineffective membrane areas respectively.
2. Osmotic Law

2.1 Content of Osmotic Law

Based on the formulas described above, we can conclude an osmotic law, i.e., in an osmotic system, osmolyte moves osmotically from the side with higher osmotic force to the side with lower osmotic force. Osmolyte(s) can be "water alone" or "water plus soluble organic compound(s) that can carry water through the semipermeable membrane". In the context of this article, we consider "water only" for the osmolyte although the osmotic law can be applied to the more complex case containing other organic compounds as the osmolytes.

Figure 1

![Image of the osmotic process](image)

(A) In the beginning of the osmosis (the initial instant of the process).
(B) In the middle of osmosis (the process is still going on).
(C) In the end of osmosis (osmotic equilibrium has been reached).

2.2 Explanation of the Osmotic Process and Membrane Morphological Change via Osmotic Law

While it was not completely satisfied to explain osmotic process with the term "osmotic pressure" due to the existence of some contradictions, it is now a perfect explanation can be done on the "osmotic process and phenomenon" with the "osmotic law" whose core concept is based on "osmotic force".
A perfect explanation for "osmotic process" can be done in the following way. In the beginning of the osmotic process, pure water (or the weak solution with lighter solute concentration) and the solution (or the solution with stronger solute concentration) have the same liquid levels on the two sides of the membrane (Fig. 1A). Nonetheless, the osmotic force is stronger on the side with pure water (having 100% of the membrane area as the osmotic effective membrane area) than the side with solution (having less than 100% of the membrane area as the osmotic effective membrane area due to solutes there). Thus, the waters in the pure water side start to permeate to the solution side causing the increase of pressure strength on that side due to the increase of the liquid level there. During this process, the osmotic force is decreasing continually on the pure water side (due to the drop of pressure strength; if in a weak solution, due to the drop in osmotic effective membrane area too from the loss of osmolyte) and the osmotic force is increasing continually on the right solution side (due to the increases in both pressure strength and the osmotic effective membrane area from the gain of osmolyte like water) (Fig. 1B). When the osmotic forces on the two sides of the membrane approach to the same magnitude where the liquid levels on the membrane two sides are stable (not going up or going down any more), the osmotic process has reached the final equilibrium state (Fig. 1C).

Once the concept of "osmotic force" is established, it is very easy to explain the law of morphological change on the membrane with non-rigid body property. On the initial instant of the osmosis (Fig. 1A) the net osmotic force on the pure water side is maximum, but the pressure strength on the two sides of the membrane is the same, so there is no elastically morphological change on the semi-permeable membrane in the macroscopic view (the elastically morphologic change of the membrane in the microscopic view, i.e., the membrane becoming thinner morphologically due to the applied pressures on the two sides, is ignored here). Following the progress of osmosis, the pressure strength is decreasing on the pure water side (on the left) and increasing on the solution side (on the right); this causes the pressure difference on the two sides of the membrane changing from none to a lot. Thus, the membrane was gradually pressed toward the pure water side due to the increasing pressure difference on two sides of the membrane (Fig. 1B). At last, the osmotic forces on the two sides of the membrane are equal (i.e., net osmotic force $\Delta F=0$) and the system is in the state of osmotic equilibrium, but the pressure difference on the two sides of membrane reaches the maximum, so the membrane is bent toward the pure water side the most at this state (Fig. 1C). What described above can explain the phenomenon as
seen on the bending of membrane shape toward the pure water side from none, small, to large degree of morphological changes.

What described above to explain either the whole osmotic process or the morphological change phenomenon of the non-rigid membrane makes perfect sense with the concept of "osmotic force". This new scientific theory is valuable because it can accomplish to logically undergo a complete and consistent description of a natural phenomenon. Furthermore, when some textbooks described and explained the osmotic process, the effect of rebound force on the membrane's elastic shape change (via the pressure difference in equilibrium) was unnoticed due to lacking the concept of "osmotic force". It was imagined, to be self-explanatory, that the pressure difference in equilibrium is due to such a huge static pressure toward the pure water side which was misunderstood as the "osmotic pressure" (4), not knowing that the force to equilibrate the osmosis on membrane two sides in osmotic equilibrium is no other forces than the equal amounts of "osmotic forces" on the two sides of the membrane. Therefore, if there is no concept such as "osmotic force" to understand its induced change and effect on the osmotic process, the interpretation and explanation of the osmotic process will no wonder be contradictory to some facts.

2.3 Osmotic Pressure Cannot Perfectly Explain the Osmotic Process

The reason "osmotic pressure" cannot be used to explain the osmotic process very well is basically because the concept of "osmotic pressure" was not derived from the dynamic process that can expose and display the whole picture and properties of osmotic phenomenon. On the contrary, it was measured via the static state which prevents the progress of osmotic process (5) (its value is the required pressure applied to the solution side liquid surface to prevent the progress of osmotic process and keep the state as in Fig. 1A). From the van't Hoff law or osmotic pressure formula \( \pi = (n/V)RT = [Ci]RT \), we can see that, besides the gas constant R and the absolute temperature T (not changed in constant condition), the osmotic pressure is proportional to the molar (quantity) concentration. Although the "osmotic pressure", being a concept to describe the osmotic process, could cover a necessary factor -- "concentration" in the osmotic process, it could not cover another necessary factor -- "pressure strength" on the membrane. Thus, it is no wonder "osmotic pressure" is not capable of explaining the osmotic process very well.
Furthermore, in the beginning of osmosis (Fig. 1A), from the viewpoint of measuring the force that can prevent the progress of osmotic process, we can see that, even if it's the same solution concentration, the force magnitude will be changing according to the different liquid levels on the membrane two sides that started changing from the same levels. This shows that the force to prevent the progress of osmotic process is not only related to concentration, but also the pressure strength on the membrane. From this, the extreme limitedness can be realized while explaining osmotic process by ignoring the pressure strength on the membrane (of course, the concept of "osmotic pressure" still have the ability to describe a general and universal property for a solution). "Osmotic force" is totally different from that; we can see clearly, from the osmotic formula $F=PS'$ or $F=PS(1-[Ci]k)$ (i.e., $S'$ is a function with respect to $[Ci]$), that "osmotic force" can cover two necessary and satisfactory factors -- "concentration" in the solution (via $[Ci]$) and "pressure strength" on the membrane (via effective area $S'$) for the progress of osmotic process. Thus, the osmotic law (described in this article), with the "osmotic force" as the core concept, can explain the osmotic process perfectly.

3. Formula for Osmotic Pressure

3.1 Logical Derivation of the van’t Hoff Osmotic Pressure Formula

van’t Hoff osmotic pressure formula was mainly implemented in the multi-phase equilibrium on chemical potential. Specifically speaking, it is based on the equilibrium of liquid and gas phases and derived by the integration of the equations for both phases. It’s summarized as follows.

When osmotic equilibrium is reached, the pure solvent side (i.e., water only A side) and solution side (i.e., the B side with impermeable solute) respectively, reach chemical potential equilibrium with the gas phase, that is:

$$\mu_A = \mu^o + RT \ln a_A + \int_{p_A}^{p_f} v_1 dp$$

$$\mu_B = \mu^o + RT \ln a_B + \int_{p_B}^{p_f+\pi} v_1 dp$$

where $\mu_A$, $\mu_B$ are the chemical potentials on the pure solvent (A) side and the solution (B) side respectively;
\( p_A, p_A + \pi \) are the pressures on two sides, \( \pi \) is the osmotic pressure among them; 
\( p^\Theta, \mu^\Theta \) are standard pressure and standard chemical potential respectively; 
\( v_1 \) is the molar volume of the solvent; 
\( a_A, a_B \) is the solvent activity on A and B sides of the membrane respectively.

Due to the equality of the chemical potentials on both solvent (A) and solution (B) sides in the state of equilibrium, i.e., \( \mu_A = \mu_B \)

Thus, 
\[
\mu^\Theta + RT \ln a_A + \int_{p^\Theta}^{p} \nu_1 dp = \mu^\Theta + RT \ln a_B + \int_{p^\Theta}^{p+x} \nu_1 dp
\]

Solve this equation followed by substitution, van’t Hoff osmotic pressure formula can be derived as: 
\[
\pi = \frac{n}{v} RT
\]

### 3.2 The Imperfection in the Logical Derivation of van’t Hoff Osmotic Pressure Formula

The above derivation, seemingly perfect, in fact, is logically seriously flawed. When osmotic equilibrium is compared to the phase change equilibrium or the chemical reaction equilibrium, there is a fundamental difference in their mechanism; the concept of “equal chemical potentials during equilibrium” can be applied for phase change equilibrium and chemical reaction equilibrium, but not for the osmotic equilibrium. Specifically speaking, in the osmotic system, the solvent and the solution have a membrane between them that can choose specific functional molecules to pass through it; and this kind of selectively permeable (semipermeable) membrane doesn’t exist among the impermeable phase change objects or chemical reactants. The two equilibrium equations seen on (1), (2) above, were based on the premise that the semipermeable membrane doesn’t exist. But after the above (3)’s derivation to (4), the existence of semipermeable membrane can be seen. In other words, van’t Hoff osmotic pressure formula is based on impermeable limiting membrane under the conditions of equilibrium as the logical premise before equation derivation, but during the derivation process, in order to meet the subjective requirement, the condition under semipermeable membrane was also set. This kind of derivation with random change on the condition is contrary to the logic that the consistency of the condition must be followed. Another point, whether phase transition
among the solid, liquid and gas three states, or allotrope (such as graphite and diamond) phase transition, there are van der Waals forces or hybrid orbital changes for the energy changes between molecules or atoms, and chemical reactions render old-bond broken and new-bond formation followed by the thermal effect of these energy changes in the process. The osmosis process is purely the diffusion movement of solvent molecules in the system; there is no thermal effect caused by energy change due to phase transition or chemical reaction. Regardless of their differences, the criterion of "equal chemical potential in equilibrium" (which are suitable for phase change or chemical reaction study), was mechanically applied as the logic of the premise to derive the osmotic pressure formula, which is inevitably biased.

It should be noted that the theoretical derivation of van’t Hoff osmotic pressure is not van’t Hoff himself but his followers who believe the formula for van’t Hoff osmotic pressure is correct. van't Hoff in 1886 found that the osmotic pressure of dilute solution could be calculated by an equation (i.e., the so called van’t Hoff osmotic pressure formula) that resembles exactly the equation to describe gas state (phase). Nonetheless, due to the far-fetched theoretical proof on the equation by the following generations, it became the so-called "semi-empirical semi-theoretical" formula. Therefore, van’t Hoff osmotic pressure formula is really just a purely empirical formula, and the lack of theoretical support for the pure empirical formula would inevitably have its limitations.

3.3 The New Osmotic Pressure Formula

Compared to the thermodynamic mechanism in phase change equilibrium or chemical reaction equilibrium, the mechanism of osmotic equilibrium is mainly reflected in the principles of hydrodynamics and membrane separation sciences. Accordingly, we use the osmotic laws based on osmotic force as the core concept to clearly derive an osmotic pressure formula with full agreement to and capable description of the ideal solution.

We start with the simplest case in order to analyze and understand. In osmotic equilibrium, if the side of the pure solvent and the membrane are same height, the liquid pressure caused by the height in the solution (B) side more than solvent (A) side is the osmotic pressure.

According to the equilibrium equation for osmotic force, we have the equation below.

\[
\text{[atmospheric pressure]} \cdot \text{[pure solvent osmotic effective membrane area]} = \text{[atmospheric pressure + osmotic pressure]} \cdot \text{[solution osmotic effective membrane area]}
\]
Above is under the ideal and standard state with solvent temperature equal to its melting temperature (for the solvent water, \( T_0 = 273.16 \text{K} \)), to describe the osmotic equilibrium in term of the equality of osmotic forces on two sides of the membrane.

However, the solvent temperature is higher than its melting point temperature in its actual state, and due to increased mobility of the solvent, the osmotic pressure on the solution side is bound to gain and the increased value depends on the ratio of thermodynamic temperature in the actual state and the thermodynamic melting point temperature of the solvent, \( \frac{T}{T^*} \), thus, based on the derivation from osmotic force equilibrium, a new formula for osmotic pressure is obtained as shown below.

\[
\pi = \left( \frac{pS'_{a}}{S'_{b}} - p \right) \frac{T}{T^*}
\]

Set \( \pi, p, S'_{a}, S'_{b}, \) and \([Ci]\) to represent “osmotic pressure”, “atmospheric pressure”, “pure solvent osmotic effective membrane area”, “solution osmotic effective membrane area”, and “solution molar concentration”; \( k \) as mentioned earlier, is the constant coefficient for the osmotic ineffective membrane areas. That is, osmotic ineffective membrane areas = \( k[CI] \)

solution osmotic effective membrane area \( S'_{b} = 1 - k[CI] \)

Based on the above osmotic pressure formula, we get the following.

\[
\pi = \left( \frac{pS'_{a}}{S'_{b}} - p \right) \frac{T}{T^*} = \left[ \frac{p(S'_{a} - S'_{b})}{S'_{b}} \right] \frac{T}{T^*} = \frac{p[1 - (1 - k[CI])]}{1 - k[CI]} \frac{T}{T^*} = \frac{pk[CI]}{1 - k[CI]} \frac{T}{T^*}
\]

i.e., \( \pi = \frac{pk[CI]}{1 - k[CI]} \frac{T}{T^*} \) \hspace{1cm} (1)

### 3.4 Different New Osmotic Pressure Formulas Derived under Different Conditions

Based on the new osmotic pressure formula (1), we can derive the following further.

(a). In osmotic equilibrium, if the hydrostatic pressure \( f \) on the pure solvent side of the membrane is higher than the membrane height, we have the following according to the osmotic force equation in equilibrium.
[atmospheric pressure + hydrostatic pressure] · [pure solvent side osmotic effective membrane area] = [atmospheric pressure + osmotic pressure + hydrostatic pressure on the opposite side] · [solution side osmotic effective membrane area]

Thus, we can derive the formula for the solution side osmotic pressure:

$$\pi = \frac{(p + f)k[C_i]}{1 - k[C_i]} \cdot \frac{T}{T'}$$ \hspace{1cm} \text{(2)}

(b) In osmotic equilibrium, if the opposite side of the solution side is not pure solvent, but with a very dilute solution with \([c_i]\) concentration and with same height as the membrane height, we have the following according to the osmotic force equation in equilibrium.

[atmospheric pressure] · [dilute solution side osmotic effective membrane area] = [atmospheric pressure + osmotic pressure] · [solution side osmotic effective membrane area]

Thus, we can derive the formula for the solution side osmotic pressure:

$$\pi = \frac{p k([C_i] - [c_i])}{1 - k[C_i]} \cdot \frac{T}{T'}$$ \hspace{1cm} \text{(3)}

(c) In osmotic equilibrium, if the opposite side of the solution side is not pure solvent, but with a very dilute solution with \([c_i]\) concentration and with hydrostatic pressure \(f\) via higher height than the membrane height, we have the following according to the osmotic force equation in equilibrium.

[atmospheric pressure + hydrostatic pressure] · [dilute solution side osmotic effective membrane area] = [atmospheric pressure + osmotic pressure + hydrostatic pressure on the opposite side] · [solution side osmotic effective membrane area]

Thus, we can derive the formula for the solution side osmotic pressure:

$$\pi = \frac{(p + f)k([C_i] - [c_i])}{1 - k[C_i]} \cdot \frac{T}{T'}$$ \hspace{1cm} \text{(4)}

The new osmotic pressure formulas shown above, i.e., (1)-(3), can be described by the new formula (4) under different conditions with \(f, [c_i]\) both 0", "\([c_i] = 0\)", and "\(f = 0\)" respectively.

In the above formula derivation, there are two negligible factors: One is that the atmospheric pressure \(p\) is also affected by temperature, i.e., the \(p\) with temperature \(T\) is

$$p_T = \int_0^\infty n m g e^{-\frac{m g}{n k T}} dx$$

, and after calculation, we know the limited change in \(T\) has little effect.
on $p_f$; thus this factor was negligible. The other one is that, in equilibrium, different heights on both sides of semi-permeable membrane make the atmospheric pressure applied on both sides a little different, but due to very minute difference, this factor was negligible too. The osmotic pressure formula intuitively comparable to van’t Hoff osmotic pressure formula is the one in (1); formula (1) is the most basic equation among a series of formulas we derived, therefore, unless under specific designation in this article, the authors refer to formula (1) for the new osmotic pressure equation.

### 3.5 The difference between the new osmotic pressure formula and van’t Hoff’s osmotic pressure formula

From the comparison between new osmotic pressure formula and van’t Hoff’s osmotic pressure formula, we know that, besides an addition to the new osmotic pressure equation in the denominator (i.e., $1 - k [C_i]$), the other parts of the new derived equation are similar to van’t Hoff osmotic pressure formula. This means that the new formula has the solution effective membrane area (i.e., $1 - k [C_i]$ which is less than 1) in the denominator, so the formula used to calculate van’t Hoff osmotic pressure would create reduced osmotic pressure than the one done by new formula. This error (subtle difference) occurs because the van’t Hoff osmotic pressure formula neglected the presence of the functional semipermeable membrane; the membrane permeability is full on the solvent side, but it is semipermeable on the solution side, so the osmosis amounts (or osmosis rate, the same below) on the solution side will be deterrent. In order to achieve equilibrium in osmosis amounts on both sides of the membrane, only under the initial basis of "equal chemical potentials", the pressure can be increased in order to eliminate the deterrent effect on the solution side, so that both sides of the membrane reached equilibrium on the osmosis amount toward the opposite side. New osmotic pressure formula has an addition in the denominator of the equation and this addition corrected the error in van’t Hoff osmotic pressure formula. By comparison of these two (old and new) formulas, we can see that the greater the concentration $[C_i]$ is, the greater error van’t Hoff osmotic pressure formula will create and the greater magnitude of correction the new formula will do. To some extent, this may also explain the correctness on the logic and conclusions for the derivation of this new osmotic pressure formula.
It can also be seen from the new formula that the osmotic pressure $\pi$ would have non-linear increase with the increase of concentration $[C_i]$, not like the linear increase as seen by van’t Hoff’s equation. In this regard, we can understand it according to the weakening of the osmotic force by the atmospheric pressure on the solution side: when the concentration difference on both sides of the membrane is very small, the effects of atmospheric pressure to cause difference of osmotic forces between both sides of the membrane are not obvious (for this reason, linear equation of van’t Hoff osmotic pressure formula is approximate to accurate only through the small concentration difference in the ideal dilute solution). However, when the concentration difference on both sides of the membrane increases, the effective membrane area on the solution side is reduced; not only original hydraulic pressure on the effective membrane area is reduced in ratio and some more osmotic force needs to be supplied to keep the equilibrium, the effect of atmospheric pressure on the effective membrane area would also be decreased in ratio too, so the overall effect of the osmotic forces on the solution side was weakened, (this is the so-called "different effects with the same atmospheric pressure" phenomenon on the two sides of the membrane, i.e., the same atmospheric pressure, but with different osmosis effects on two sides of the membrane), and this needs some “supplemented” to maintain the equilibrium. And this "supplemented" part must be for osmotic pressure to bear. On this point, we just need to take a look at the following osmotic force equilibrium equation and it can be clearly understood.

$$\text{[atmospheric pressure]} \cdot \text{[pure solvent osmotic effective membrane area]} = \text{[atmospheric pressure + osmotic pressure]} \cdot \text{[solution osmotic effective membrane area]}$$

It can be seen from the above equation that, when the solution side concentration increases, "the solution side osmosis effective membrane area" is reduced; in order to maintain osmotic equilibrium, the whole item of \([\text{atmospheric pressure + osmotic pressure}]\) in above equation would increase proportionally; not only the "osmotic pressure" but also the “atmospheric pressure“ should be increased in proportion, but the "atmospheric pressure" is a fixed value and can not be increased, so "osmotic pressure" would play this extra heavy task of “increasing” duty. Especially with the increasing concentration on the solution side, the steady decline in the effective membrane area would become increasingly large and show accelerated. This accelerated reduction in effective membrane areas can only be compensated by the
simultaneous acceleration of osmotic force increase to maintain the osmotic equilibrium, which is reflected by the increasing growth rate of osmotic pressure with the increase of concentration [Ci] in the solution side.

**3.6 Mathematical Proof for the Characteristics of the New Osmotic Pressure Formula**

Characteristics of the new osmotic pressure formula can be further proved from the mathematical point of view.

To get novelty osmotic pressure formula, let’s start from first derivative \( \pi' \) and second derivative \( \pi'' \) for the function

\[
\pi = \frac{p k [C_i]}{1 - k [C_i]} \cdot \frac{T}{T'}
\]

\[
\pi' = \frac{d \pi}{d [C_i]} = \frac{p k (1 - k [C_i]) - p k [C_i] (-k)}{(1 - k [C_i])^2} \cdot \frac{T}{T'}
\]

\[
= \frac{p k (1 - k [C_i] + k [C_i])}{(1 - k [C_i])^2} \cdot \frac{T}{T'} = \frac{p k}{(1 - k [C_i])^2} \cdot \frac{T}{T'}
\]

\[
\pi'' = \frac{d}{d [C_i]} \left( \frac{d \pi}{d [C_i]} \right) = \frac{p k \cdot 2 (1 - k [C_i]) (-k)}{(1 - k [C_i])^4} \cdot \frac{T}{T'} = \frac{2 p k^2}{(1 - k [C_i])^3} \cdot \frac{T}{T'}
\]

Because \( p, k, T, T' \) are positives, so inside the function domain \( [0, \frac{1}{k}] \), \( \pi' > 0 \rightarrow \pi'' > 0 \). Thus, not only we can determine the original function’s characteristic, i.e., the unidirectional accellerated increments and the image of the function curve bent upward for the osmotic pressure formula (1), \( \pi = \frac{p k [C_i]}{1 - k [C_i]} \cdot \frac{T}{T'} \) (see figure below), but also that the second derivative \( \pi'' > 0 \) prove the unidirectional accelerated increase for the first derivate \( \pi' \). That is, with the concentration increasing, there comes the accelerated increase of the osmotic pressure.

Similarly, from the first and second derivatives on formulas (2), (3), and (4), we can reach the same conclusions.
3.7 To Fully Understand the Characteristics of New Osmotic Pressure Formula from its Equation’s Function Curve

Let’s set \( p, k, T, T' \) to constants, so we can further discuss the function curve of the new osmotic pressure formula (1), \( \pi = \frac{p k [Ci]}{1 - k [Ci]} \cdot \frac{T}{T'} \), to clearly explain the characteristic that the increase of the osmotic pressure was accelerated with the increase of the concentration \([Ci]\).

In formula (1) above, \( p \) is the atmosphere pressure, \( T \) is the thermodynamic temperature under the actual state of experimental condition, \( T' \) is the solvent's thermodynamic melting temperature, and \( k \) is the equilibrium constant (equivalent to \( R \) in the dilute ideal solution), being the fraction of the ineffective membrane area as described in the above sections "Osmotic Force and "Osmotic Law". \( \frac{T}{T'} \) is an adjustment ratio reflecting the increase of the osmotic pressure, which is caused by the effect of increased experimental temperature on the solvent.

As proved earlier with first and second derivative calculations, equation (1) is related to an ascending curve concave upward as seen in Figure 2. It can be seen that the curve is close to linear in dilute (low) concentration solutions; the linear curve in this part is close to the linear equation for van't Hoff osmotic pressure formula, i.e., \( \pi = [Ci]RT \), but theoretically equation (1) is more accurate than the linear equation. When the solution is in much higher concentration range, the increase of the osmotic pressure is accelerated as seen from the curve concave upward in Figure 2. This turns out to be a perfect match between scientific facts and theory when equation (1) is applied, and this overcomes the limitedness of van't Hoff osmotic pressure formula for ideal dilute solution only.

From the discussion above about Figure 2, we can see why the van’t Hoff osmotic pressure formula is only applicable to dilute ideal solutions. Only in an ideal dilute solution and the concentration difference on both sides of the membrane is very small, the osmotic pressure and concentration can show a linear equation relationship; and van’t Hoff equation, \( \pi = \frac{n}{v}RT \), at certain fixed temperature, has concentration as a function of the linear equation, so it can only be used to approximate the ideal dilute solution. But the new osmotic pressure formula is a curve equation; in the more dilute concentration it shows a straight line relationship, while the concentration is large, it shows the curved relationship to match perfectly with the actual osmosis.
mechanism. So the new formula for osmotic pressure helps us fully understand the nature of the osmotic process via the law observed between solution concentration and osmotic pressure.

![Figure 2](image)

The plot for the change of osmotic pressure ($\pi$) versus the change of solute concentration [Ci] according to the formula in equation (1) if $p=1$ atm, $k=0.0224$ (derived from the R value for dilute ideal solution), and $\frac{T}{T'}=1$. When the [Ci] is low (e.g., less than 10 moles/liter), the curve is almost linear; the linear curve in this part is close to the linear equation for van't Hoff osmotic pressure formula, i.e., $\pi = \frac{n}{V}RT$ or $\pi = [Ci]RT$.

**Conclusion**

The scientific history told us about the current scientific concepts that, as said by Einstein, "they will be removed if they cannot be properly legitimated, corrected if their correlation with given things be far too superfluous, and replaced by others if a new system can be established that we prefer for whatever reason" (6). This is the necessity for the continual growth of scientific knowledge. Although related to the interpretation of the osmotic process, the concept of "osmotic pressure" seems too "loose" now and it should be and must be replaced with the new concept of "osmotic force" or "osmotic law" discussed herein.
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