

That the Ratio of Osmotic Pressure to Freezing-Point Depression Is Constant Follows from an Assumption, Not from a Measurement

— **13.153443** for All Four Solutes — But the Content Lies Elsewhere, in the Assumption That One and the Same Particle Count Enters Both, and That Can Break by **6.95** Per Cent — [Paper 333]

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September 2026

— *From thinking to syncing.* —

Abstract

Osmotic pressure and freezing-point depression are both said to depend only on the number of particles, never on what the solute is. This paper asks how much of that “sameness” has actually been measured—the answer is that the constancy itself follows from an assumption, and what is measured is the assumption. No new mathematical theorem and no new law is claimed. First, $\pi/\Delta T_f$ is **13.153443** atm/K for all four solutes (Section 2). Second, this is the core of the paper. That constancy follows from putting the same i into both, and is not an independent measurement (Section 3). Third, so the test must be recast into a form that can fail. Let i differ as 2.00 against 1.87 and the ratio moves by 6.9519 per cent (Section 3). Fourth, putting the measured i (for sodium chloride, 1.87) into both leaves the ratio where it was (Section 4). Fifth, the ratio does not move with the solute and does move with the solvent and the temperature. In camphor it is 0.0465 of the value in water; at 373.15 K it is 16.462208 (Section 4). Sixth, the separator is whether the solute was changed or the solvent was (Section 5).

Scope of this paper (scope note): No new mathematical theorem and no new law is claimed——van 't Hoff's law, freezing-point depression, colligative properties, and the van 't Hoff factor i are all standard. We do not build solution theory——Debye-Hückel theory and the computation of activity coefficients are not entered. They are mentioned and no more. We perform no experiment——the measured values of i used here are taken from the literature and were not measured by the author. What is calculated and what is quoted are marked apart. We do not treat concentrated solutions——only the dilute formulae are used; departures at high concentration are not the subject. We do not line up boiling-point elevation or vapour-pressure lowering——there are four colligative properties; only two are compared here. We do not treat biological membranes——the practice of semipermeable membranes and cellular osmoregulation is not entered. Relation to earlier papers: Paper 300 showed whether two things share a root is decidable——this paper is a record of that test applied to one actual case. And it shows that applying it as “the ratio is constant, therefore one root” is not, as it stands, a test at all. Paper 268 showed that the triple point being a point is not an experimental fact——the same shape, a case where what looks like a measurement follows from a convention or a definition. Paper 95 separated convention from fact——the ratio here sits on the side of how the formulae were written, not on the side of fact. Paper 326 showed the square-cube law to be an identity——the same warning: do not read what cancels as “agreement”. Paper 316 showed the same integer returning from three different counts——there the counts were independent. The two here are not. What is added is making explicit that the constancy is a cancellation, giving in numbers how the ratio moves when i is displaced, so that the test can fail, confirming that measured values of i leave the ratio unmoved, and putting the separator on solute against solvent.

1. Notation and the Question

Setting: Dissolve a solute in a solvent. Two things happen.

Phenomenon	Formula	What occurs
Osmotic pressure	$\pi = imRT$	solvent is drawn across a semipermeable membrane
Freezing-point depression	$\Delta T_f = iK_fm$	the freezing temperature falls

Observation 1.1

Both are explained as “fixed by the number of particles, whatever the solute is”. They are called colligative——if one phrase explains both, perhaps they come from one root.

Observation 1.2

Paper 300 laid down three criteria for deciding whether two things share a root. One of them is whether the ratio stays constant as the variables are moved——this paper applies it.

Observation 1.3

The way of measuring is fixed first. $R = 0.08205737 \text{ L}\cdot\text{atm}/(\text{mol}\cdot\text{K})$, $T = 298.15 \text{ K}$, $K_f = 1.86 \text{ K}\cdot\text{kg}/\text{mol}$ for water, and $m = 0.5 \text{ mol}/\text{kg}$ ——the dilute formulae are used as they stand, without distinguishing molarity from molality.

Question: Do the two come from one root, and how would one confirm it?

2. Four Solutes, and the Ratio Does Not Move

Calculation 2.1: Compute π and ΔT_f for four solutes that dissociate differently (computed in this paper).

Solute	i	π [atm]	ΔT_f [K]	$\pi/\Delta T_f$
Sucrose	1	12.2327	0.9300	13.153443
Sodium chloride	2	24.4654	1.8600	13.153443
Calcium chloride	3	36.6981	2.7900	13.153443
Aluminium sulfate	5	61.1635	4.6500	13.153443

Observation 2.2

A check——the same formula gives seawater (about 1.1 mol/kg of total ions) an osmotic pressure of **26.9119 atm**, inside the usual 25 to 27 atm. And 0.5 molal sodium chloride depresses the freezing point by 1.8600 K, as expected——two independently known cases are tried before the table is read.

Observation 2.3

i runs from 1 to 5 and the right-hand column does not move one digit. π goes from 12.2327 to 61.1635, fivefold, and ΔT_f moves with it——only the ratio stands still.

Calculation 2.4: The same under a change of concentration (computed in this paper).

Concentration m [mol/kg]	$\pi/\Delta T_f$ (sodium chloride)
0.1	13.153443
0.5	13.153443
1.0	13.153443
2.0	13.153443

Observation 2.5

Concentration does not move it either. Applied naively, the criterion of Paper 300 gives one root on all three rows——stop here and one could write that a common root has been shown.

3. The Core: That Constancy Is a Cancellation, Not a Measurement

Setting: Write the ratio in symbols.

Observation 3.1

Dividing the definitions gives

$$\frac{\pi}{\Delta T_f} = \frac{i m R T}{i K_f m} = \frac{R T}{K_f},$$

so both i and m cancel——the ratio does not move with solute or concentration because neither survives on the right.

Observation 3.2

This is the core of the paper. The table in Section 2 measures nothing—compute RT/K_f directly and it is **13.153443**, the same value as all four rows. Listing four solutes does no evidential work.

Observation 3.3

The test in Section 2 could not have failed. Whatever solute is brought, whatever i may be, the ratio is bound to be RT/K_f —a test certain to pass says nothing when it passes.

Observation 3.4

So where is the content? The cancellation was possible because the same i was put into both—the assumption that “the number of particles setting the osmotic pressure” and “the number setting the freezing-point depression” are the same number: that is the claim.

Calculation 3.5: Break the assumption. Displace the two values of i and see the ratio (computed in this paper).

i (osmotic side)	i (freezing side)	$\pi/\Delta T_f$	Departure
2.00	2.00	13.153443	0.0000 per cent
2.00	1.90	13.845729	+5.2632 per cent
2.00	1.87	14.067853	+6.9519 per cent
1.87	2.00	12.298469	−6.5000 per cent

Observation 3.6

Now the test can fail. A discrepancy of 6.5 per cent in i moves the ratio by 6.9519 per cent—measure the ratio to one per cent and a discrepancy in i is detectable at the one per cent level. Only here does the verdict of common root acquire content.

Observation 3.7

The direction reverses too. 2.00 against 1.87 gives +6.9519; 1.87 against 2.00 gives −6.5000—the sign says which side has the greater particle count.

4. Even the Measured i Leaves the Ratio Unmoved

Setting: Real values of i are not integers, because ions do not become entirely free.

Calculation 4.1: Take literature values near 0.5 molal. These values of i were not measured by this paper; they are the accepted figures.

Solute	Ideal i	Approximate measured i	Shortfall
Sucrose	1	1.00	0.00 per cent
Sodium chloride	2	1.87	6.50 per cent
Calcium chloride	3	2.60	13.33 per cent

Observation 4.2

The more charge the salt carries, the greater the shortfall. 0.00, then 6.50, then 13.33 per cent—because the ions attract one another and cease to behave independently.

Calculation 4.3: Put these measured values of i equally into both formulae (computed in this paper).

Solute	i	π [atm]	ΔT_f [K]	$\pi/\Delta T_f$
Sucrose	1.00	12.2327	0.9300	13.153443
Sodium chloride	1.87	22.8752	1.7391	13.153443
Calcium chloride	2.60	31.8050	2.4180	13.153443

Observation 4.4

π and ΔT_f both fall 6.5 per cent below the ideal, and the ratio does not move one digit. Because both columns fall by the same amount—the ratio does not know the value of i . All it knows is whether the two are using the same one.

Observation 4.5

So this ratio is no instrument for counting particles. To learn the number one must measure π or ΔT_f singly and extract i —what the ratio answers is not a quantity but an identity.

Calculation 4.6: What, then, does move it (computed in this paper)?

What is changed	Value	$\pi/\Delta T_f$
Solvent (water)	$K_f = 1.86$	13.153443
Solvent (acetic acid)	$K_f = 3.90$	6.273180
Solvent (benzene)	$K_f = 5.12$	4.778399
Solvent (camphor)	$K_f = 40.00$	0.611635
Temperature 273.15 K	water	12.050521
Temperature 373.15 K	water	16.462208

Observation 4.7

In camphor it is 0.0465 of the value in water. A quantity that did not move one digit across four solutes falls to a twenty-first of itself when the solvent changes—what the ratio carries is a property of the solvent, not of the solute.

5. The Separator: Was the Solute Changed, or the Solvent?

Observation 5.1

The separator——whether the quantity moved lies on the side that cancels or on the side that survives.

	Symbol	Effect on the ratio	What it tells
Solute, concentration	i, m	cancels	nothing
Solvent, temperature	K_f, T	survives	the value of the ratio

Observation 5.2

The separator is not on the side of the phenomena but on the side of how the formulae were written. The same experiment, the same solution——what survives in the ratio and what cancels was settled by how the two expressions were assembled.

Observation 5.3

The criterion of Paper 300 needs mending in how it is applied. “Does the ratio stay constant as the variables move” is right, but it spins idly unless one says which variables——moving a variable that cancels and reporting “it stayed constant” is a test that could not have failed.

Observation 5.4

To be stated honestly——that the two do share a root is probably true. Both follow from the chemical potential of the solvent being lowered by the solute——what this paper says is not “they have distinct roots” but “the table in Section 2 is not evidence for it”. A conclusion and the support for a conclusion are separate things.

Observation 5.5

Where this stands relative to Paper 268. Paper 268 wrote that the triple point being a point is not an experimental fact—there too, what looked like a measurement came out of a convention. Here what looked like an agreement comes out of a cancellation.

Observation 5.6

One last thing—when the same number appears, the first thing to suspect is one's own formula. Four solutes agreeing to six decimal places looked like strong evidence—and the perfection of the agreement was itself the signal that nothing had been measured. Two measurements never agree to six decimal places.

6. The Census and the Close

1. **13.153443** for four solutes (Calculation 2.1): *i* ran from 1 to 5.
2. **26.9119** atm for seawater (Observation 2.2): the usual **25** to **27** atm.
3. Concentration does not move it (Calculation 2.4): **0.1** to **2.0** mol/kg.
4. RT/K_f computed directly is also **13.153443** (Observation 3.2): *i* and *m* cancel.
5. Section 2 could not have failed (Observation 3.3): certain to pass from the start.
6. **2.00** against **1.87** gives **+6.9519** per cent (Calculation 3.5): now it can fail.
7. Measured *i* for calcium chloride is **2.60** (Calculation 4.1): **13.33** per cent below ideal.
8. Measured *i* leaves the ratio unmoved (Calculation 4.3): both fall equally.
9. Camphor gives **0.0465** of water (Observation 4.7): a twenty-first.
10. **16.462208** at **373.15** K (Calculation 4.6): proportional to absolute temperature.

Closing: Osmotic pressure $\pi = imRT$ and freezing-point depression $\Delta T_f = iK_fm$ are both said to depend only on the number of particles and never on what the solute is—and indeed $\pi/\Delta T_f$ comes to **13.153443** atm/K for all four solutes, which dissociate quite differently, and does not move one digit as the concentration runs from 0.1 to 2.0 mol/kg. Applied naively, the criterion of Paper 300 gives one root on all three rows. And yet that constancy measures nothing—written in symbols the ratio is RT/K_f , so both *i* and *m* cancel. Computed directly, RT/K_f is **13.153443**. Whatever solute is brought, the ratio is bound to take that value; the test could not have failed, and a test certain to pass says nothing when it passes. The content lies in the fact that the cancellation was possible at all—it was possible because the same *i* was put into both, and the claim is precisely that the number of particles

setting the osmotic pressure and the number setting the freezing-point depression are one number. And that can break—let i differ as 2.00 against 1.87 and the ratio moves **6.9519** per cent; reverse the direction and it moves -6.5000 , the sign saying which side carries more particles. Putting the measured values of i into both leaves the ratio where it was—1.87 for sodium chloride and 2.60 for calcium chloride pull π and ΔT_f below the ideal, but they fall by the same amount and the ratio stays at **13.153443**. The ratio does not know the value of i ; all it knows is whether the two use the same one. What does move it is the solvent and the temperature—camphor gives **0.611635**, a mere 0.0465 of water, and 373.15 K gives 16.462208. A quantity unmoved across four solutes falls to a twenty-first of itself under a change of solvent. What the ratio carries is a property of the solvent, not of the solute. One thing separates them—whether the quantity moved lies on the side that cancels or on the side that survives. The separator is not in the phenomena but in how the two formulae were assembled. To be said honestly—that the two share a root is probably true. Both follow from the chemical potential of the solvent being lowered by the solute. What this paper says is not “they have distinct roots” but “the table in Section 2 is not evidence for it”. A conclusion and the support for a conclusion are separate things. One last thing—when the same number appears, the first thing to suspect is one’s own formula. Four solutes agreeing to six decimal places looked like strong evidence. The perfection of the agreement was itself the signal that nothing had been measured. Two measurements never agree to six decimal places.

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