



Philosophical Magazine Series 5

ISSN: 1941-5982 (Print) 1941-5990 (Online) Journal homepage: <http://www.tandfonline.com/loi/tphm16>

XII. Intelligence and miscellaneous articles

S. U. Pickering F.R.S.

To cite this article: S. U. Pickering F.R.S. (1894) XII. Intelligence and miscellaneous articles , Philosophical Magazine Series 5, 37:224, 162-164, DOI: [10.1080/14786449408620530](https://doi.org/10.1080/14786449408620530)

To link to this article: <http://dx.doi.org/10.1080/14786449408620530>



Published online: 08 May 2009.



Submit your article to this journal [↗](#)



Article views: 3



View related articles [↗](#)

TABLE II.

Hydrochloric acid	100
Trichloroacetic acid	68
Dichloroacetic acid.....	23
Monochloroacetic acid	4.3
Acetic acid	0.35
Biboric acid	0.0057
Hydrocyanic acid.....	0.0026
Carbolic acid	0.00094
Carbonic acid	0.00091

The numbers attached to each acid cannot of course be considered final. As regards carbolic and carbonic acid, for example, it is impossible to say which of the two is the stronger, all that we may safely infer is, that they are about equally strong.

From the above table it also follows that hydrochloric acid is about one hundred thousand times stronger than carbolic acid in tenth-normal solution ; or, what amounts to the same thing, the electrolytic dissociation ratio is one hundred thousand times greater in the former case than in the latter.

In other tables of the avidities of acids the values for the weakest acids are usually represented by blanks, but the method which has just been described enables us to arrange them in proper order and to assign definite values to them.

This seems all the more necessary as a great deal of misconception still prevails as to the relative strengths of the acids and the conditions under which a comparison is possible.

University College, London. .

XII. *Intelligence and Miscellaneous Articles.*

ON THE FREEZING-POINTS OF SODIUM-CHLORIDE SOLUTIONS.

BY S. U. PICKERING, F.R.S.

IN a recent communication to the *Phil. Mag.* (xxxvi. p. 484) Mr. Harry Jones has made sundry very incorrect statements as regards a controversy respecting the regularity or otherwise of the freezing-points of weak sodium-chloride solutions. I should not have troubled to correct them had Mr. Jones inserted any reference to the communication which has apparently closed this controversy (*Ber. d. deutsch. chem. Gesell.* xxvi. p. 1977), and which must have been in his hands before he corrected the proofs of his paper for this Journal.

In the *Berichte* (xxv. p. 1314) I published a series of determinations with this salt which I considered indicated the presence of

changes of curvature at certain points. Mr. Jones subsequently published (*Ber.* xxvi. p. 551) some still more accurate determinations, which he considered entirely disproved the existence of these breaks. I proved, however (*Ber.* xxvi. p. 1221), that, so far from this being the case, Mr. Jones's results showed the very same breaks as mine did, but in a still more satisfactory manner. I proved that parabolas deduced mathematically from his values so as to allow the existence of these breaks agreed most perfectly with the known experimental error as determined by two independent methods, whereas, when represented by a single parabola without breaks, the error was 10,000 times too large. Mr. Jones found it convenient to ignore the results of this investigation in his answer (*Ber.* xxvi. p. 1635), which may be summarized in his own words in the *Phil. Mag.* "I have carefully examined his [Pickering's] results . . . and have shown that the 'breaks' are caused only by the experimental errors in his results. Mr. Pickering has applied his method of curve-drawing to my results from sodium chloride, which differ from his to the extent of more than 50 per cent., and with it claims to have found the same 'breaks' as in his own results. He has thus shown the true value of his method, which seems to be largely independent of the experimental data. I have since shown that his curve contains the following fundamental errors:— I. At least some of the points in his curve are wrong. II. The choice of points through which he has drawn the curve is purely arbitrary."

It is true that I *did* examine Mr. Jones's results by drawing curves through them, but, as I never published the results, I fail to see how he can pretend to know anything about them, unless it is from a rough woodcut on p. 1222 of the *Berichte*. His answer, which does not, and evidently could not, apply to the mathematical investigation, appears to me to be calculated simply to shirk the results of this investigation, which are too conclusive to be withstood. His statement that my results differ from his by at least 50 per cent. may be characterized by your readers as they think fit. The sole foundation for it is that in the one extreme experiment, and in that only, there is such a difference, and that there it amounts to but 0.002° C., an error of which many of Mr. Jones's duplicate results are by no means innocent.

Mr. Jones's "careful examination" of my results consisted of displaying some of them in a woodcut in a manner which would inevitably fail to reveal anything as to their true nature, and his "proof" of the regularity of his own results consists of a similar plotting. I can only repeat in English what I have already told him in German (*Ber.* xxvi. p. 1979), that so long as he offers no evidence to invalidate that which I have brought forward in favour of the irregularity of these results, and so long as he declines to give the smallest proof whatever to support his statement that they form a regular curve, I must decline to discuss the matter any further.

I am tempted, however, to say a word as to Mr. Jones's recent results, although it is impossible to attempt a criticism of them till the

experimental values, instead of the present "smoothed" values, are published. The most remarkable part of the conclusions which he draws from them is that non-electrolytes in very weak solutions give an abnormally large depression similar to that given by electrolytes, but which according to the dissociation theory should be shown by electrolytes only. It is still more remarkable, however (especially when we remember that these results emanate from Prof. Ostwald's laboratory), that Mr. Jones should have published them without any reference to the fact that my own results (although they differ somewhat from his in individual cases) had established the existence of this same phenomenon, not only as regards aqueous solutions, but still more conspicuously as regards benzene solutions (*Ber.* xxiv. pp. 1469, 3329; xxv. pp. 1854, 2011, 2518, 3434).

Mr. Jones suggests a possible explanation of this excess in the case of non-electrolytes, without noticing, however, that it must apply equally to electrolytes also, and thus upset the very conclusions which he has drawn from the rest of his work, namely, that the excess is due to dissociation and agrees accurately with the electric conductivity. Perhaps I may help him a little out of his difficulty by suggesting that, after all, part of this 25 per cent. excess may be due to experimental error. When a student whose work is hitherto unknown publishes results which claim an accuracy ten times greater than any previously attained, it is but reasonable to expect fuller details than those given by Mr. Jones. A mercurial thermometer reading with certainty to the ten thousandth of a degree is an instrument unknown in England, and any systematic investigation of its capabilities would add confidence to our estimate of the results obtained. Independent of errors due directly to the thermometer, I should like to ask if Mr. Jones has satisfied himself that he gets the same value for the freezing-point of water (on which all his conclusions depend) whatever method he uses for determining it. In his apparatus the sides and bottom of the vessel are being constantly cooled by the surrounding medium, the top is being constantly heated by partial contact with the air, and the contents are being heated by the friction of the stirrer. When freezing begins, the liquid can only be kept at the same temperature as the ice if this latter is disseminated throughout it in considerable quantity and in minute particles; but, according to my experience, this is almost impossible when dealing with a large bulk of pure water, even when violently stirred: the ice forms and agglomerates on the sides of the vessel, leaving the liquid in the middle to become superheated and give too high a reading for the freezing-point. A similar phenomenon occurs to a less extent with very weak solutions, and gradually becomes negligible as the strength increases, and as the ice which separates forms in smaller crystals which do not agglomerate so easily. An error due to this cause would account for the very high values obtained by Mr. Jones for weak solutions.