

SOME BOILING-POINT DETERMINATIONS

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Quite recently there appeared a paper by Freyer¹ on the boiling-points of solutions containing alcohol, sugar and water. He found that when the amounts of the two solutes were expressed in volume concentrations, the presence of sugar lowered the boiling-point instead of raising it. If, however, the concentrations of the alcohol and sugar are given in grains per liter, the concentration of the water necessarily changes with changing amounts of sugar. Of more importance is the fact that the ratio of alcohol to water increases with increasing concentration of sugar and the lowering of the boiling-point might be due chiefly to that. In order to settle the question I have made several measurements with the Orndorff apparatus, adding alcohol and then sugar to a constant quantity of water. In all cases the boiling-point rose on adding sugar. The experiments were then repeated, substituting sodium chlorid for sugar. The result was the same as in the preceding case.

It seemed desirable to determine the effect, if any, of the presence of alcohol on the change of boiling-point due to the addition of salt. Since salt and alcohol are not miscible to any appreciable extent, one effect of adding salt must be to increase the partial pressure of the alcohol vapor and therefore to diminish the rise of boiling-point and to increase the apparent reacting weight. On the other hand it has already been shown² that the decrease in the partial pressure of the solvent due to the presence of two solutes is greater than the sum of the changes due to each solute when the solutes are non-miscible. The effect of this would be to increase the

¹Zeit. angew. Chem. **1896**, 654.

²McIntosh, Jour. Phys. Chem. **1**, 474 (1897).

boiling-point and to diminish the apparent reacting weight of the sodium chlorid. At present there is no way of predicting which of these effects will be the greater and it seems not impossible that in some cases the one might predominate and in others the other.

My measurements with sodinm chlorid are given in Tables I-II. Opposite the word alcohol is given the amount of this substance in one kilogram of water and the lowering of the boiling-point actually observed. The values K and M are calculated from the formula $\frac{g}{\Delta} K = M$, taking $M = 58.5$ when calculating K and $K = 0.520$ when calculating M. Under g is the amount of sugar in grams per kilogram of water and under Δ is given the rise of boiling-point measured from the boiling point of the alcohol-water mixture as zero.

TABLE I

Barometer. 745.3 mm

Alcohol 8.37 g = -0.450°

g	g/M	Δ	K	M
2.79	0.048	0.040°	0.838	36.3
5.36	0.092	0.060	0.655	46.5
10.21	0.175	0.130	0.745	40.8
14.38	0.246	0.190	0.773	39.4
21.74	0.372	0.300	0.807	37.7
30.56	0.522	0.450	0.861	35.3
43.02	0.736	0.640	0.869	35.0
54.45	0.925	0.840	0.908	33.5

In the first series there was very little alcohol and the effect would therefore be correspondingly small. If we omit the first determination, in which the percentage error is very large, we see that the apparent reacting weight of sodium chlorid decreases regularly from about forty-six to thirty-three. If sodium chlorid were completely dissociated, and there were no disturbing factors we should get an apparent reacting weight of a little over twenty-nine and a value $K = 1.04$. It is clear that, in this particular case, the

TABLE II

Barometer. 741.5 mm

Alcohol 18.53 g = — 1.585°

g	g/M	Δ	K	M
8.54	0.146	0.065°	0.446	68.2
19.69	0.337	0.155	0.45	66.1
33.68	0.575	0.295	0.513	59.3
42.30	0.723	0.425	0.587	51.8
59.41	1.016	0.595	0.586	51.9
73.77	1.262	0.765	0.607	50.1
88.69	1.486	0.935	0.630	48.3
106.65	1.824	1.145	0.628	48.4
123.39	2.006	1.365	0.647	47.0

presence of alcohol increases the apparent reacting weight and that this effect diminishes as the ratio of salt to alcohol increases. In the second series the effect of the alcohol is much more marked, the apparent reacting weight of the sodium chlorid being higher in the first three measurements than it would be if sodium chlorid were a non-electrolyte and no alcohol were present. This disposes of the criticism which might have been urged against the first series, that the increase in the apparent reacting weight was due to a decrease in dissociation caused by the addition of alcohol.

One set of measurements was made with sugar and eighty per cent alcohol. The first addition of sugar produced an apparent lowering of the boiling-point but the change is so small, 0.005°, that no stress is to be laid upon it. Further addition of sugar caused a rise of the boiling-point. This rise is so small that if the alcohol were ignored and only the ratio of sugar to water were taken into account we should find an apparent reacting weight of five to six thousand for sugar. This of course means nothing and is merely a striking instance of the precipitation of alcohol by sugar. The data are given in Table III. Under g_1 are grams of sugar in one kilogram of aqueous alcohol; under g are grams of sugar in one kilogram of water and under Δ the changes of boiling-point, a rise being considered positive.

TABLE III

Barometer. 743.0 mm

g_r	g	Δ	g_r	g	Δ
15.8	63.2	-0.005°	97.8	391.2	0.030°
29.6	118.4	$+0.000$	113.9	455.6	0.040
44.3	177.2	0.010	127.6	510.4	0.050
57.9	231.6	0.020	138.7	554.8	0.060
68.6	274.4	0.025	152.6	610.4	0.060
82.1	328.4	0.030			

Cornell University ; May, 1897.