

## ON THE SYSTEM WATER, PHENOL, AND HYDROCHLORIC ACID

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Phenol and water form a partially consolute mixture. If the temperature be sufficiently lowered, solid phenol separates and we have a two-component system with two liquid phases, a solid phase and a vapor phase, and complete equilibrium at a definite temperature. The addition of hydrochloric acid, which is very soluble in water, but slightly soluble in phenol changes the relative miscibility of the two original components and the temperatures at which solid phenol can exist in the altered system is raised. We will now have a ternary system with a solid phase, two liquid phases, and a vapor phase, consequently one degree of freedom, and since neither the water nor hydrochloric acid can separate in the solid phase, the system may not become non-variant so long as the phase liquid phenol persists.

But the case under consideration can be made to assume special features. If we keep the mass of phenol *relatively* small, water is so little soluble in it, that as the solid phenol separates, the concentration of the water hydrochloric acid is but slightly changed, and the freezing temperature of the phenol remains very constant in a similar manner to the case which Nernst has already described.<sup>1</sup>

Qualitatively, the case under consideration has been specifically discussed by Bancroft<sup>2</sup> in a study of ternary systems with two liquid phases, and he found that solid phenol was in equilibrium with liquid phenol and water at  $+0.8^{\circ}$ , whereas the temperature rose to about  $25^{\circ}$  when the laboratory acid, presumably

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<sup>1</sup> Zeit. phys. Chem. 6, 30 (1890).

<sup>2</sup> Jour. Phys. Chem. 1, 420 (1897).

a concentrated solution, was used in place of the water. These figures must have been determined as rough approximations, however.

In the experiments here described, we measured the temperatures at which solid phenol separated from its melt in contact with aqueous solutions of hydrochloric acid. The conditions under which the measurements were made, were not the ideal ones suggested by *a priori* considerations. It was soon found to be impracticable to have the volume of water large in comparison with the volume of phenol present. The apparatus used was essentially that of the "Beckmann Freezing-point Method" with slight modifications, but we made it smaller and more compact than usual, materially increasing the convenience and time elements in its use. In stirring the mixture when large amounts of water were used, it was not possible to prevent the phenol from freezing in detached masses throughout the water solution, when its entire mass very rapidly became solid, an undesirable result in itself, and the thermometer registered absolutely noncomparable and confusing readings conditioned by the supercooled water solution. The thermometer was of the Raoult type for freezing-point determinations, gave direct readings on the centigrade scale, and was graduated to tenths, hundredths being readily estimated. The recorded readings on the means of from four to five determinations in each case, the direct variations not exceeding  $0.03^{\circ}$  in any case. The hydrochloric acid solutions were all made from c. p. acid and distilled water and compared by titration against a very carefully prepared  $\left(\frac{N}{5}\right)$  sodium hydroxid solution. The titrations were all made *after* the freezing-point determinations, and any possibility of obtaining prejudiced readings was avoided. The phenol was purified by repeated distillation, first and last portions of the distillate being discarded. It distilled at a constant temperature. It was kept in a flask with a tight-fitting stopper carrying a calcium chlorid drying tube, and when needed, was melted by careful warming, the desired portion being rapidly transferred to the

freezing-point apparatus. The hydrochloric acid was at once added, but cautiously, to such amount as somewhat more than saturated the phenol. The thermometer was so adjusted that the bulb was entirely covered by the liquid phenol. The determination was made in the usual manner. The first reading obtained was always discarded, being used simply as an indication as to how far the solution should be undercooled, about  $0.3^{\circ}$  being the amount of undercooling we considered allowable. The results obtained are given in the following table:

Gms. per liter 0.0000	Reacting wts per liter 0.0000	Freezing- point $1.365^{\circ}$	Gms per liter for $1^{\circ}$ rise 0.000	Rise of freez- ing-point per reacting wt $\infty$
0.8035	0.0222	1.737	2.159	16.75
1.6154	0.0446	1.883	3.118	11.61
3.4028	0.0941	2.298	3.647	9.91
4.1574	0.1149	2.443	3.856	9.38
8.3009	0.2294	3.048	4.932	7.33
13.1323	0.3629	4.000	4.983	7.26
16.2384	0.4488	4.738	4.814	7.52
21.9251	0.6060	5.603	5.173	6.99
32.8514	0.8965	7.100	5.728	7.51
66.2671	1.8316	12.013	6.223	5.81
130.9690	3.6199	17.078	8.335	4.34
131.3234	3.6297	17.195	8.296	4.36

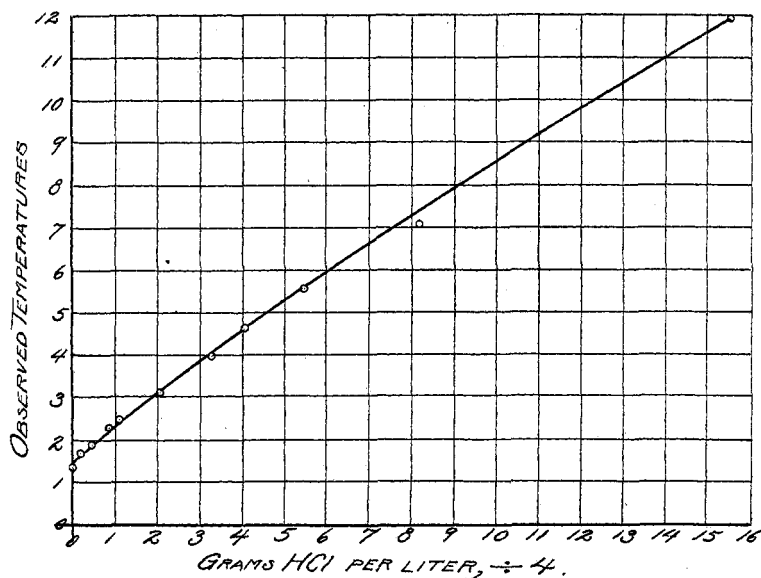
With hydrochloric acid in excess, the freezing-point of the phenol<sup>1</sup> was  $25.26^{\circ}$ .

The first column gives grams of hydrochloric acid per liter of solution. The second reacting weights of hydrochloric acid per liter. The third, the observed temperature readings. The fourth, the number of grams hydrochloric acid per liter corresponding to a rise of  $1^{\circ}$  in each case. The fifth, the rise of temperature corresponding to one reacting weight per liter of solution, in each case.

These results are indicated on the accompanying chart. It has seemed desirable to select grams hydrochloric acid per liter as abscissæ, and for convenience in illustrating, they are divided

<sup>1</sup> The phenol used melted at  $40^{\circ}$  C and distilled constantly at  $176.5^{\circ}$  C.

throughout by four. The ordinates represent the corresponding temperatures found. The curves, even as charted, and especially that part illustrating the lower concentrations, is quite flat, approximating a straight line. But the fourth column of the table shows undoubtedly a curvature exists. The fifth column shows that the curve would be of practically the same nature if



plotted with reacting weights as coordinates. The upper part of the curve appears to approach parallelism to the axis of abscissæ.

It has been suggested by Bancroft that this method be used for standardizing hydrochloric acid solutions, thus doing away with the tedious weighings, filterings, etc. involved in the usual procedure. By reference to the fourth column it will be seen that the accuracy of the method is dependent on the concentration.

For solutions about  $\left(\frac{N}{10}\right)$  tenth-normal, it will be seen that an error of  $0.01^\circ$  corresponds to less than 0.04 gram per liter. But we are convinced from our experience, that even in the hands of an expert, it is not safe to assume a less error than  $0.02^\circ$

in determining unknown solutions, unless indeed unusual care be observed and a thermometer reading to thousandths of a degree be used. Therefore, while the method should prove a useful and rapid one for making up solutions of approximately known strength, it is not sufficiently refined for the requirements of good analytic practice. And in consequence, it did not seem worth while to standardize our thermometer, or to attempt a further and more accurate determination of the curve.

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