A STUDY OF THE TEMPERATURE OF THE VAPOR

ABOVE A BOILING SALT SOLUTION

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By John Andrew Palm

Approved by Charles B. Hurd

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HISTORICAL

The temperature of the vapor over a boiling saline solution has been stated by Michael Faraday[1] to be the same as the boiling temperature of the pure solvent. However, Gay Lussac and Wulner[2] believed the temperature of the vapor to be the same as the temperature of the solution from which the vapor was evolved. Neither Faraday nor Gay Lussac seemed to have done extensive experimental work on this subject in order to find exactly what the temperature of the vapor is.

Since that time quite a bit of work has been done on this problem, all of which was divided into the two schools of thought; that presented by Faraday and the one by Gay Lussac. No one seemed to believe that the vapor temperature might be something other than that of the boiling solvent or solution itself. K. Schreber[3] experimented and found his results to agree with the work of Faraday, but I. Pollitzer[4], O. Knoblauch and F. Reiher[5], Balke and Wilson[6], and E. von Reissmann[7] found that they agreed with the statement of Gay Lussac. At Union College James Rice[8] in 1926, E. S. Bartlett in 1929 and Leo W. Scott in 1931 worked on the problem. Both Rice and Bartlett found their results to agree in general with the statement of Faraday. Scott's work did not.

An interesting account of how Faraday and Gay Lussac arrived at their opinions on the subject was given by G. Harker[9] in 1920.

In 1822 Faraday found that in his experiments when the bulb of a thermometer was sprinkled with salt and introduced into steam the temperature recorded was greater than 100° C.; the steam generated from a boiling salt solution had only the temperature of 100° C.

Gay Lussac differed with Faraday on theoretical grounds. He considered that the vapor must have the same temperature as the liquid with which it is in contact.

Later on Faraday published a paper in which he proved the contentions of Gay Lussac to be correct.

The one work at Union College which seemed to give fairly positive results was that of Bartlett[10]. He attempted, by means of certain conclusions of A. Berthaud, Briner, and A. Schidlof[11] about the Ebullescopic Paradox, to show theoretically that Faraday's first contention was correct. They believed that the work done against osmotic pressure in changing the concentration of the solution accounts for the difference in temperature between the vapor and solution. The formation of vapor at 109° C. from a boiling saturated salt solution actually requires less heat than the formation of the same amount of vapor at 100° C. from boiling water.

APPARATUS

The apparatus used in these experiments was designed primarily to prevent: (1) the cooling of the vapor once it had been evolved; (2) the heating of the vapor after it had been evolved; (3) splashing of solution on the thermometer. There is a possibility of radiation to or from the thermometer, but this radiation would have been negligible in any case.

The first two objectives to overcome were eliminated by the use of a quart Dewar which was silvered. The vacuum gave excellent insulation to the solution which the Dewar contained. The Dewar being made of Pyrex glass prevented any heat flow from the solution to its vapor by conduction through the walls of the Dewar. This entire Dewar was then placed in a water thermostat kept at a fairly high temperature of around 80° C.

A clearer description of the complete apparatus can be made by referring to the accompanying drawings.

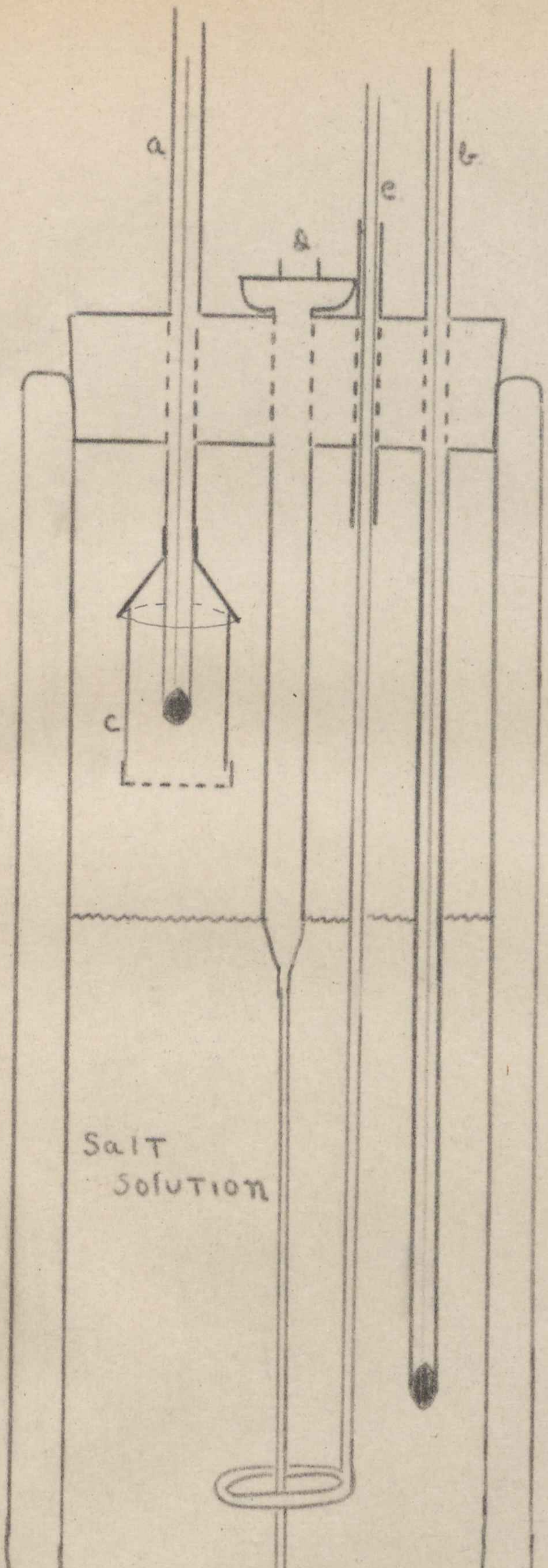
In Figure I is pictured the Dewar alone. An electric knife heater (a) was used to heat the solution up to boiling, and a circular glass rod (b) surrounding the heater, when operated by hand by pushing it up and down, acted as a stirrer to keep the solution homogeneous, as well as to prevent the salt from caking out onto the heater, where the solution bubbled onto it. A 110° C. thermometer (c) immersed into the solution, so that the bulb of the thermometer was about half the way down into the solution, showed the steady rise of the solution temperature.

In order to prevent splashing of solution and condensation of vapor on the thermometer, a salt trap was designed which would eliminate both of these points.

Referring to Figure II: A piece of sheet copper (a) was cut in the shape of a cone, so that it would slide onto the thermometer and protect the bulb of the thermometer from vapor condensation which would ordinarily run right down onto the bulb and give a false reading of the vapor temperature. This operates in the same way as a person is sheltered from the rain by an umbrella. A piece of glass tubing (b) about 12 mm. inside diameter and about 5 cm. long was then put over the bulb of the thermometer and fastened to the copper shelter by means of steel wire and heat and moisture proof cement. The bottom of the glass tube which was opened was covered with a fine mesh bronze screen(c). The screen permitted the free access of the vapor to the bulb, but at the same time prevented any solution to splash onto it.

Figure III is a complete drawing of the entire apparatus when in operation.

Vapor from the boiling solution escaped freely to the atmosphere through the stirring rod tube.



a Vapor Therm.

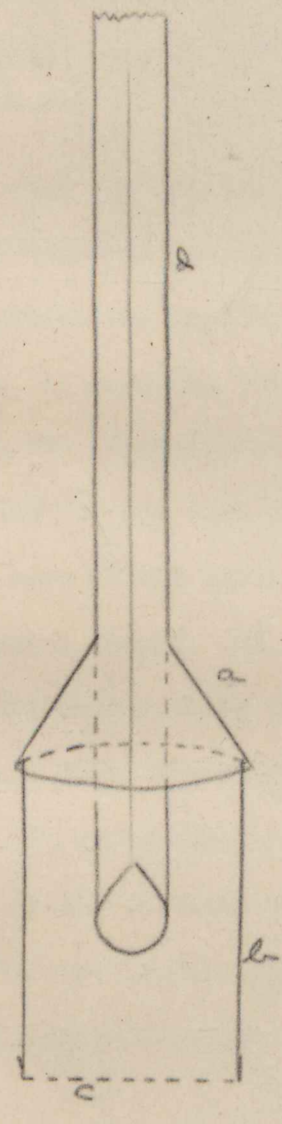
b... Solution Therm.

c... Salt Trap

d... Knife heater

e... Stirring rod

Figures I and III



a---Copper shield

b---Glass Tube

c---Wire screen

d---Thermometer.

Figure II

THEORETICAL

The various features which this apparatus consists of should now be explained as to their function in showing that the vapor temperature over a boiling saline solution is the same as the vapor temperature over the pure boiling solvent.

As to heat flow from the boiling solution through the walls of the Dewar; this flow of heat I think is insignificant with this apparatus in spite of the fact that if two systems are in thermal contact, they will tend to become of equal temperature. If anything this heat flow should raise the temperature of the vapor, but the experimental data showed the vapor temperature to rise until it reached 100° C. and then remained constant. The only other source of heat other than that of the vapor reaching the thermometer would have been radiation from the heater itself. Of course there was nothing to prevent this from occuring, but caution was taken to see that the heater was well immersed into the solution;and since the vapor temperature remained at 100° C. while the solution boiled, it was naturally thought that there was no significant amount of radiation being absorbed by the thermometer from the heater. Since the salt trap and thermometer were exposed directly only to the vapor, there was no chance of any appreciable heat flow to the thermometer from other sources.

Extreme care was taken with the construction of the salt trap,for this part of the apparatus was the piece that kept the vapor from condensing upon the thermometer,in which case the temperature registered would have been that of the condensed vapor, and therefore could not have been any higher than the boiling point of the pure solvent. The explanation of the construction of the salt trap was given in a previous section of this treatise; and so no space will be devoted to that here. The only proof to ascertain whether the salt trap did successfully what it was intended to do was to remove the thermometer immediately from the vapor, after a run, and observe whether there was any condensation on the bulb or not. There was no evidence at all that condensation had taken place during the run. The bulb was even touched with the tongue to see if any solution had splashed through the screen on the salt trap and onto the thermometer,in which case a higher temperature than 100° C. would have been observed if the splashing was appreciable.

EXPERIMENTAL

I. The outer vessel or thermostat was filled with water and heated by flame until the temperature of the water was near boiling or 100° C. The vessel was then removed from the flame and two electric knife heaters were placed into the water and the water then let come to a constant temperature, as shown by a thermometer placed in the water especially for this purpose.

II. The Dewar containing the salt solution stopper, heater and thermometer were then placed in the water and held there rigidly by a metal sleeve fastened to the thermostat. A cover was placed over the apparatus, leaving exposed only the scales on the thermometer, and the plugs of the heaters, which were connected to the 110 v. laboratory source. As the solution was heated by the heater, recordings of it's temperature were taken as well as the temperature of the atmosphere above the solution. Then when boiling started, temperatures of both vapor and solution were continued to be recorded for a time to see if they varied from constant values. In every case both the vapor temperature and the solution temperature seemed to reach their maximum values at about the same time.

III. At the completion of the run the stopper holding the thermometer and heater from the Dewar, was removed and the salt trap slipped away from the bulb of the thermometer, which was then examined for any condensation or traces of salt. Neither ever seemed to have formed at all on the thermometer.

CONCLUSION

Summary of Results and Critique of Method

The results obtained with the apparatus seemed to be quite conclusive that the temperature of the vapor above a boiling salt solution is the same as the temperature of the pure solvent.

The salt trap was successful in doing what it was designed to do. It prevented solution splashing on the thermometer bulb, and it prevented condensation of the vapor on the bulb of the thermometer.

The fact that at all times the temperature of the thermostat was not the same indicates that probably the thermostat was not necessary, and the vacuum contained between the walls of the Dewar was sufficient insulation to prevent any heat flow either from or to the solution through the Dewar.

If no serious fault has been overlooked in the apparatus, the following conclusions can be drawn.

The temperature of the vapor above a boiling salt solution is the same or close to that of the pure solvent.

The vapor was not cooled after escape from the solution. If there was any temperature change in the vapor at all it must have been an increase.

Some Concluding Remarks

Finally, it might be suggested that with this same apparatus, solutions of salt in some organic solvents such as CCl_4 and C_6H_6 be tried and determine whether the same results are obtained.

DATA ON RUNS

			B. P.	Ice point
Calibration -	Thermometer used in vapor	No. 1	100.0° C.	0°
	Thermometer used in solution	No. 2	100.1° C.	0°
	Thermometer used in thermostat	No. 3	99.9° C.	3°

Run	Molarity	No. 1 Initial v. t.	No. 2 Initial sol. t.	No. 3 Initial therm. t.
1	3 M	78.5° C.	91.5° C.	64.0° C.
2	3 M	60.5° C.	74.9° C.	60.0° C.
3	3 M	68.4° C.	73.8° C.	62.0° C.
4	sat'd. sol.	99.6° C.	106.0° C.	78.0° C.
5	sat'd. sol.	98.5° C.	101.5° C.	79.0° C.
6	sat'd. sol.	96.0° C.	100.0° C.	84.0° C.

Run	Molarity	Final v. t.	Final sol. t.	Final therm. t.
1	3 M	100.1° C.	104.9° C.	64.0° C.
2	3 M	100.6° C.	105.4° C.	59.0° C.
3	3 M	100.0° C.	104.5° C.	61.0° C.
4	sat'd. sol.	101.0° C.	110.2° C.	79.0° C.
5	sat'd. sol.	100.0° C.	109.0° C.	79.0° C.
6	sat'd. sol.	100.0° C.	108.8° C.	84.0° C.

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