

mixture over cobaltous oxide in the temperature range of 330 to 570° in the above experiments.

5.  $\Delta F_{1373}^{\circ}$  for the formation of cobaltous oxide from cobalt and oxygen has been calculated by combining the free energy change involved in forming water vapor from hydrogen and oxygen with that found experimentally in the present research for the reduction of cobaltous oxide to cobalt by hydrogen. A value of 32,050 calories so obtained yields a value of  $0.5 \times 10^{-7}$  mm. for the partial pressure of oxygen in equilibrium with CoO-Co mixture at 1100°, that is, in agreement with Foote and Smith's failure to detect measurable dissociation of cobaltous oxide at that temperature.

6. The temperature of transformation of hexagonal to cubic cobalt has been fixed as lying between 340 and 360°.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF MICHIGAN]

## AN APPARATUS FOR TESTING DÜHRING'S LAW FOR CORRESPONDING BOILING POINTS

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RECEIVED JUNE 3, 1929

PUBLISHED NOVEMBER 8, 1929

### Introduction

In 1877 Dühring<sup>1</sup> found that a linear relation existed between the boiling temperatures of two liquids boiling under the same pressures. So far this law has been tested indirectly by plotting corresponding boiling points from vapor-pressure data obtained for the two liquids separately. If the two liquids could be boiled in different parts of a closed system, then as the pressure is varied in the system, the corresponding boiling temperatures could be observed directly. This was tried out and it has given satisfactory results. The apparatus is of simple construction and is easy to manipulate.

### Discussion

The apparatus is illustrated in Fig. 1. Bulbs are blown at the bottom of two upright reflux Liebig condensers. At the top the condensers are connected to each other and to a vacuum pump, which may be an ordinary aspirator. In the latter case a water trap should be provided in the evacuating train. In order to condense the vapors of the boiling liquids at low temperatures ice water should be led through the condensers.

The liquids to be boiled are poured into the bulbs to about the level indicated in the figure. Porous plate or bisque fragments are added to minimize bumping. The boiling temperatures are obtained by two

<sup>1</sup> Dühring, *Wied. Ann.*, 11, 163 (1880).

thermometers entering the bulbs through necks on the bulbs. Airtightness is secured by pieces of rubber tubing fitting over the thermometers and the necks. A cloth gasket is desirable in the case of an organic liquid in order to minimize contact of the liquid with the rubber.

The heating may be done by small flames of Bunsen burners. The bulbs containing the liquids are shielded by asbestos sheets having small holes in the center to permit local concentrated heating and thus help to reduce bumping.

In actual operation it is best to evacuate first and start the liquids boiling at low temperatures and to let a slow leak into the apparatus gradually raise the boiling temperatures. Another advantage of starting at low temperatures is that the liquids are then most likely to bump, but the pores of the porous plate contain then more air than later and are thus more effective in reducing bumping. The air leak may be controlled by a screw clamp over a rubber tubing on the exhaust tube. The temperatures may be read conveniently at degree intervals. A continuous rise in temperature of  $1^\circ$  in three to five minutes is found to be slow enough for accuracy. When the pressure is back to atmospheric, it may be carried a little above by admitting compressed air at low enough pressure so as not to endanger the apparatus.

The observed temperatures have to be corrected for the length of the mercury thread exposed to room temperature. This correction is to be added to the reading of the thermometer. It is expressed by the formula

$$C = 0.00016 \times l_{\text{Hg}} (t - t_R)$$

where  $l_{\text{Hg}}$  is the length of the exposed mercury column in degrees,  $t$  is the reading of the thermometer and  $t_R$  is the room temperature.

The apparatus was tried out for benzene and ethyl alcohol against water. The equation of the corresponding boiling-point curve for alcohol was found to be

$$t_A = -12.23 + 0.9062 t_W \quad (1)$$

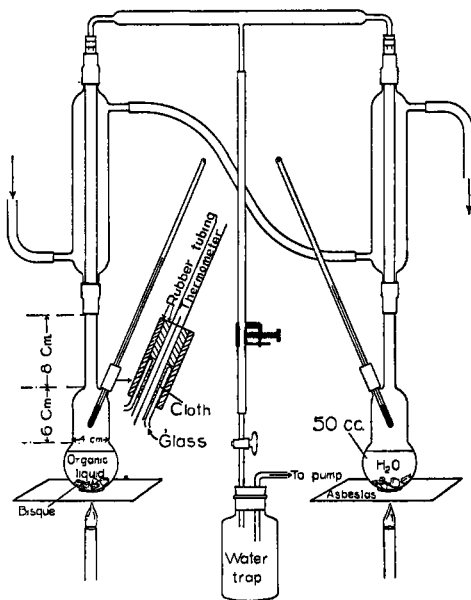


Fig. 1.

The maximum deviation of observed readings from this relation was less than  $0.07^\circ$  in absolute value and nowhere was there a trend toward either algebraic sign of the deviations. The boiling temperature at one atmosphere calculated from the equation is  $78.39^\circ$ . The value given in "International Critical Tables," Vol. III, p. 217, is  $78.32^\circ$ .

The results obtained for benzene do not follow a single linear relation so well; they form a curve slightly concave upward. The data may, however, be represented closely by three line segments, each holding for part of the curve. From  $54$  to  $70^\circ$  on the water axis the line

$$t_B = -30.49 + 1.0948 t_W \quad (2)$$

holds, from  $70$  to  $90^\circ$  the line

$$t_B = -32.39 + 1.1222 t_W \quad (3)$$

and from  $90$  to  $105^\circ$  the line

$$t_B = -34.77 + 1.1491 t_W \quad (4)$$

The maximum deviations of observed values from these lines was less than  $0.08^\circ$  in absolute value. The boiling point of benzene at one atmosphere therefore is  $80.14^\circ$ . Smith and Menzies<sup>2</sup> found it to be  $80.12^\circ$ . Both the benzene and alcohol were of high purity and were used for molecular weight determinations. The experiment for the benzene was repeated with another sample and practically the same results were obtained.

Figure 2 represents the data graphically. In Table I are shown some vapor-pressure values of alcohol and benzene as calculated from Equations 1, 2, 3 and 4 and a reliable table of the vapor pressure of water. The corresponding values found by others are also given in the table for comparison.

TABLE I

## RESULTS

Temp., °C.	Vapor pressure in mm. of mercury			
	Alcohol	Crit. tables <sup>a</sup>	Benzene	Smith and Menzies (Ref. 2)
35	102.7	103.7	148.14	...
40	135.2	135.3	182.5	...
45	172.5	174.0	223.3	...
50	220.6	222.2	270.5	...
55	279.5	280.6	325.6	...
60	352.4	352.7	390.1	...
65	437.5	438.8	464.9	463
70	540.7	542.5	549.7	551
75	664.0	666.1	646.3	650
80	809.5	812.6	756.7	757.5
85	981.0	986.3	...	...

<sup>a</sup> "International Critical Tables," Vol. III, p. 217.

<sup>2</sup> Smith and Menzies, THIS JOURNAL, 32, 1448 (1910).

Any inherent errors in the apparatus are present in both halves, and if the two temperatures are close together, these errors largely cancel each other. To make this more certain the two halves of the apparatus should be as nearly alike as possible. High-grade thermometers of the same type should be used.

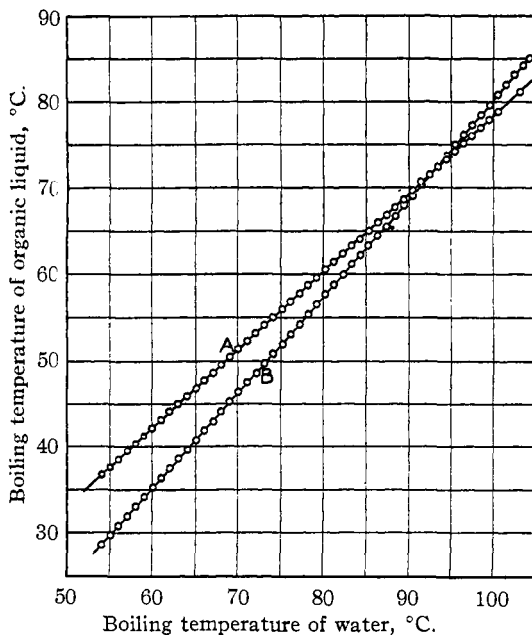


Fig. 2.—A, Ethyl alcohol; B, benzene.

This apparatus as shown is applicable only to pure liquids, where the vapor has the same chemical composition as the liquid, not to solutions or mixtures, where this is not in general, true.

### Summary

An apparatus was developed for testing Dühring's law of corresponding boiling points. It was tried out for benzene and ethyl alcohol. The law was found to hold for the alcohol over the range observed but not for the benzene.

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