hydrogen fluoride appear to be somewhat less than corresponding salts in water. Thus calcium and magnesium fluorides are less soluble in hydrogen fluoride than are the oxides in water, etc. Chromium fluoride seems to be an exception to this conclusion.

Summary

1. The solubility of lithium hydrogen fluoride between 0 and 40° has been established, and zinc fluoride, magnesium fluoride and calcium fluoride have been shown to be very insoluble. Potassium iodide has been found to react with liquid hydrogen fluoride. Chromium fluoride was found quite soluble but to an undetermined extent. These solubilities refer to liquid hydrogen fluoride as a solvent.

2. Comparison of these results indicates a fair similarity in the solvent action of water and hydrogen fluoride for the salts tried.

IOWA CITY, IOWA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING OF THE STATE UNIVERSITY OF IOWA]

A METHOD FOR THE DETERMINATION OF CRITICAL TEMPERATURES AND THE CRITICAL TEMPERATURE OF HYDROGEN FLUORIDE

BY P. A. BOND AND DELLA A. WILLIAMS

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Accurate determination of the critical temperature by the usual method is difficult for several reasons. In the first place, glass is a poor conductor of heat and slight differences in bath temperature are not readily transmitted to the substance through the necessarily thick walls. Also for the same reason one end of the tube may be of slightly different temperature than the other. The gas above the critical temperature is very dense, diffusion is relatively slow and equalization of conditions in the tube does not readily take place. Some substances such as hydrogen fluoride attack glass and some such as nitrogen peroxide are so intensely colored at the critical temperature that observation is exceedingly difficult. The liability of tubes exploding under high pressures has also been a real difficulty where greater pressures are encountered. The method noted below permits the determination to be made without danger to the operator and under conditions of greater accuracy than those obtainable when the glass tube is used. Monel metal was used in the determinations because of its resistance to the action of hydrofluoric acid. Other metals could be used in the construction if desired.

Description of Apparatus

The critical temperature apparatus was composed of a constant temperature oven (Z), an assay balance (Y) and a critical temperature tube (D)

(see Fig. 1). The critical temperature oven (Z) had an insulation of asbestos between the inner transite compartment (X) and the outer wooden box. The cover to the box was similarly insulated with asbestos. The heat was supplied by a resistance coil of nichrome wire (H). Circulation of the air inside was obtained by the use of the fan (A_1) propelled by the motor (A), the speed of which was regulated by a bank of lamps. After the oven had been heated for four hours and the heat and fan then turned off, a drop of but half a degree per minute was recorded. The readings were obtained from the thermometers E and E_1; one was placed in the corner of the oven and the other directly above the critical temperature tube.

The balance (Y) had the pan rests taken off, and a hole drilled through the base. At one end of the balance beam a platinum wire (F), size 50, was attached. The wire extended to the tube (D) and was of such length that the tube rested at an angle of about 20 degrees to the horizontal.

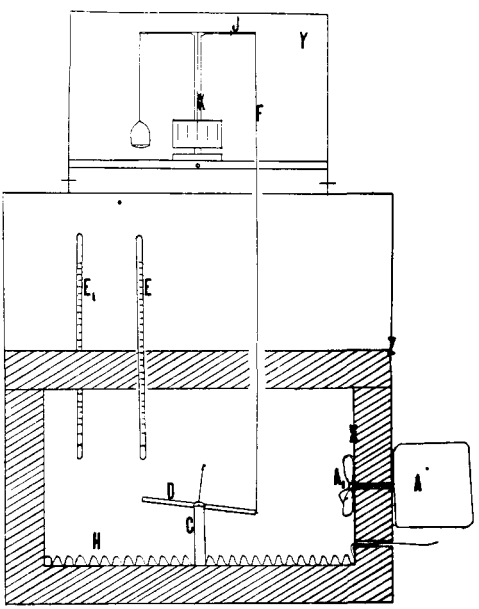

Fig. 1.

The critical temperature tube (see Fig. 2) was 153 mm. long, 10 mm. diameter, with a wall 1 mm. in thickness. It was supported on steel knife edges (S) which rested on the polished surface of the support (C). The pointer (R), carrying the slide (V), was used to regulate the sensitiveness of the balanced system. A gold washer (U) was used to prevent leakage around the screw (T).

Manipulation

The critical temperature tube had a capacity of 1.88 cc. To insure that the tube was approximately half full of liquid, it was weighed after each filling. In order to be certain that there were no small leaks, the tube was allowed to stand for twelve hours and reweighed. If a constant weight was obtained, the tube was placed in the constant temperature oven. The oven had been heated previously, with the fan running, from three to four hours. The platinum wire was attached to the end of the tube and the oven again heated to above the critical temperature for more than an hour to insure constant temperature and uniform density of the gas within the

tube. Differences in densities have been found to exist in the case of pure substances, above the temperature at which the meniscus disappears. According to Hein[1] in the case of pure carbon dioxide at 0.46° above the critical temperature seventy minutes elapsed after the disappearance of the meniscus before an equalization in density resulted.

When the thermometer read about 300° the fan and heat were both turned off. The system was balanced with the rider (J). When cooling had occurred to the critical temperature, the formation of the liquid phase in the lower end of the tube set the pointer of the balance in motion. The critical temperature was read at the first movement of the pointer.

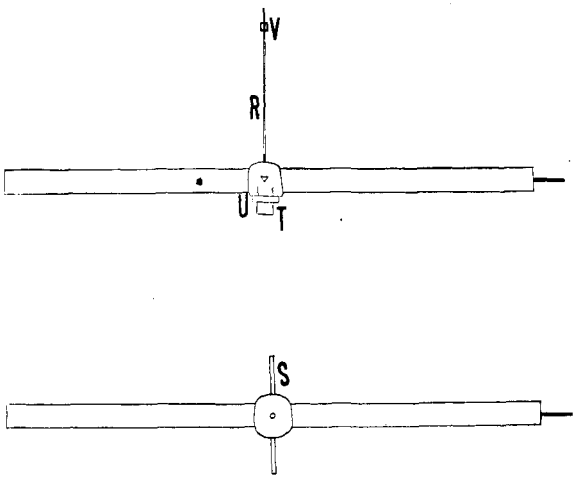

Fig. 2.

The apparatus was checked using sulfur dioxide prepared according to the method employed by Stephens[2] and others in this Laboratory. The hydrofluoric acid was prepared by the method of Stowe.[3]

Results

The critical temperature of sulfur dioxide was found to be 157.8°. This temperature checked in two tubes of the anhydrous liquid. Critical temperatures of sulfur dioxide determined previously were

155.4	Sajatschervsky[4]	157.15	Cardoso Bell[4]
156	Cailletet, Mathias[4]	157.6	Niggli[4]
157.26	Centnerszwer[4]	157	Drion[5]
157.20	Briner[4]	159	Sandenburg[5]
157.3	Travers[4]		

[1] Hein, *Z. physik. Chem.*, **86**, 385–426 (1914).
[2] Bond and Stephens, THIS JOURNAL, **51**, 2910 (1929).
[3] Bond and Stowe, *ibid.*, **53**, 30 (1931).
[4] "Phys. Chem. Tabellen," **1923**, p. 261.
[5] "Physico-Chem. Tables," **1911**, Vol. I, p. 544.

The critical temperature of hydrogen fluoride was determined by this method. The tube was filled with fresh samples of the anhydrous liquid three times, and the following results were obtained

	Reading 1	Reading 2
First filling	230.2°	230.2°
Second filling	230.2	230.2
Third filling	230.0	....

Van Laar calculated the critical temperature of hydrogen fluoride using the formula[6]

$$\frac{T_c}{T_b} = K$$

Using $K = 1.7$, which is the average value of K as calculated from experimental values for hydrogen chloride, hydrogen bromide and hydrogen iodide

$$T_b = 292.5°\text{A.} = 19.5°\text{C.}$$

Substituting in $T_c = KT_b$

$$T_c = 497°\text{A.} = 224°\text{C.}$$

Substituting the observed critical temperature of hydrogen fluoride in the formula

$$\frac{T_c}{T_b} = K$$

we get the value $K = 1.72$, which is close to the observed values for hydrogen chloride, hydrogen bromide and hydrogen iodide.

Summary

A new method for the determination of the critical temperature has been developed. It may be used for substances which attack glass, and for those like nitrogen dioxide, where a meniscus cannot be observed. The critical temperature of anhydrous hydrogen fluoride was found to be 230.2°.

The value of K in the formula $T_c/T_b = K = 1.72$ for hydrogen fluoride is very close to the average value as calculated from the observed boiling points, and critical temperatures of hydrogen chloride, hydrogen bromide and hydrogen iodide.

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[6] Van Laar, *J. chim. phys.*, **18**, 273–282 (1920).