[Contribution from the Chemical Laboratory, The Johns Hopkins University]

CRITICAL TEMPERATURE MEASUREMENTS ON CARBON DIOXIDE IN SMALL CAPILLARIES[1]

By Harvey Thomas Kennedy

Received October 10, 1928 Published May 6, 1929

Patrick and McGavack[2] have established the relation between the quantity of gas adsorbed by silica gel and the equilibrium pressure, as follows

$$V = K\left(\frac{\sigma P}{P_0}\right)^{1/n}$$

where V is the volume of liquefied gas at the prevailing temperature and pressure, σ the corresponding surface tension, P is the equilibrium pressure, P_0 is the ordinary saturation pressure and K and n are constants. This equation has been used to correlate measurements of adsorption in silica gel with the vapor pressures of sulfur dioxide and ammonia by Patrick and Davidheiser,[3] of butane by Patrick and Long[4] and of nitrous oxide and carbon dioxide by Patrick, Preston and Owens.[5] The latter writers made measurements of adsorption both above and below the critical temperature and concluded that liquid exists in the pores of the adsorbant above the critical temperature, as ordinarily measured in large tubes. Thus they believe that liquid carbon dioxide exists in the pores of silica gel at 40°, about 9° higher than the previously reported critical temperature.

While it is perhaps impossible to test this hypothesis directly, that is, by actual observation of a liquid phase within the fine pores of an adsorbent, it was thought that if the hypothesis were in accord with the facts, some increase in critical temperature should be observed in very fine glass capillaries, even though the diameters of the capillaries were many times those of the finest pores in silica gel. The work here described was undertaken largely to determine what relation, if any, exists between the diameter of small capillaries and the critical temperature of material measured in them.

Carbon dioxide was chosen for this work because its critical point is conveniently near to room temperature and because it is easily obtained in a state of high purity.

The first attempt to determine the effect which diameter of capillary had on the critical temperature consisted in the construction of the apparatus shown in Fig. 1 which contains carbon dioxide adjusted to critical volume. When the temperature is raised slowly from slightly below the

---

[1] Dissertation submitted to the Board of University Studies of Johns Hopkins University, in conformity with the requirements for a degree of Doctor of Philosophy.

[2] McGavack and Patrick, This Journal, **42**, 946 (1920).

[3] Davidheiser and Patrick, *ibid.*, **44**, 1 (1922).

[4] Patrick and Long, *J. Phys. Chem.*, **29**, 336 (1925).

[5] Patrick, Preston and Owens, *ibid.*, **29**, 421 (1925).

critical to slightly above, it was expected, if the diminishing diameter had the effect of raising the critical temperature, that the meniscus would appear in the tube D and slowly move from the upper and larger end to the lower and smaller end. Conversely, as the temperature is lowered, the opposite motion should be observed.

As impurities in the carbon dioxide might give the same effect as described above, without the diameter itself having any effect, the greatest care was exercised in preparation and purification.[6]

Figure 2 shows diagrammatically the apparatus by which the carbon dioxide was further purified and conducted into the tube shown in Fig. 1 by multiple sublimation.

Before the purification was completed, no measurable pressure was indicated on the McLeod gage when liquid air was placed under either I or J, and the sublimation into it completed, the stopcock O being closed.

The behavior of the meniscus was then observed by placing the tube D before a microscope, the optical axis of which was horizontal, and which was so arranged that it could be moved up and down, thus allowing the tube to be viewed throughout its length. A mercury thermometer graduated in 0.01° was placed at the side of the tube D, and the room temperature was varied very slowly and regularly by means of a large fan and gas flames placed a considerable distance from the apparatus.

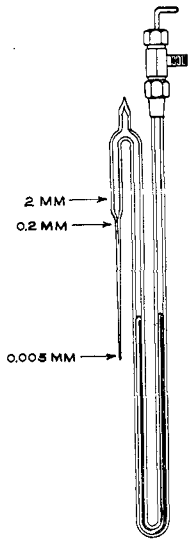

Fig. 1.

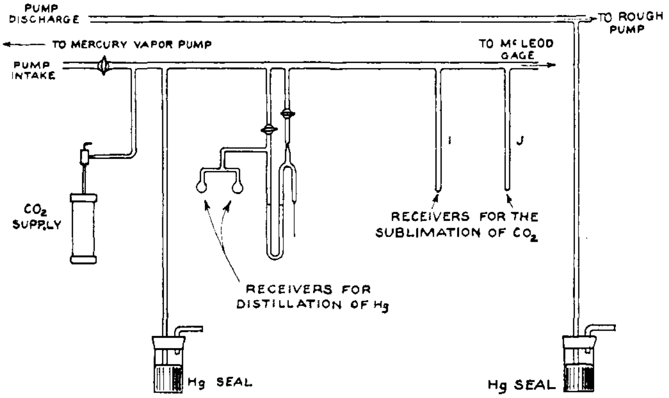

Fig. 2.

The result predicted by the hypothesis explained at the beginning of this paper, namely, that the meniscus should move downward in the tube D as

---

[6] For a detailed description of the generation and purification of the carbon dioxide used in this investigation, see Meyers and Van Dusen, *Refrigerating Eng.*, **13**, 180 (1926).

the temperature was raised, and *vice versa,* was not observed since no meniscus was observed in the small tube D at any time, although the temperature was raised above the critical and lowered many times, and various schemes of illumination tried.

It was then decided that the negative result obtained was not entirely conclusive. The meniscus, if present in the very fine tube would be difficult to see, and great delicacy in temperature control might be necessary to hold it at any point in the tube for a long time. It was, therefore, decided to make determinations of the critical temperature of carbon dioxide in very fine capillaries of different diameters and to compare these values with those obtained in larger tubes.

To make and fill these tubes, essentially the same apparatus was used as is shown in Fig. 2, the fine tubes being made by heating the ends of tubes I and J, drawing out to the required internal diameter and, after filling, collapsing until adjusted to critical volume.

These small tubes were drawn as described for two reasons: first, the ratio of surface to volume in them was very great as compared to tubes in which critical temperatures have previously been determined, and small quantities of adsorbed gases on the glass walls would have a much greater effect; second, previous work has shown that the action of water on soft glass essentially changes its surface, and irregularities thus caused might interfere with observations of critical temperature. It is believed that with freshly drawn tubing, which has never been in contact with any gas except carbon dioxide of high purity, both of these difficulties are overcome.

The apparatus for the determination of the critical temperatures of carbon dioxide in the small tubes is shown in Fig. 3.

Temperature regulation was secured by the 40-watt lamp I, which was connected to a line the voltage of which could be varied in 11-volt steps. External resistance in series with the lamp was also provided so that fairly rapid or very slow rates of heating could be obtained. The lamp was surrounded with a section of a cone, made of black paper, with a disk of the same material on its top so perforated that the direct radiation from the lamp did not fall upon the contents of the Dewar tube.

Illumination was secured by a 200-watt tungsten lamp set beyond the Dewar tube at an angle of about 30° with the optical axis of the microscope. Between the Dewar tube and the lamp was placed a large bottle of water so as to shield the water in the Dewar from the heat from this source. It was found that the very small tube could best be observed by moving the microscope objective somewhat further away from the tube than the position corresponding to sharp focus and observing a greatly enlarged pattern formed only when an angle of approximately 30° existed between the optical axis of the microscope and the line from the lamp to the Dewar tube. In this pattern liquid and vapor were differentiated as light and dark bands, and could be clearly distinguished, especially when moving, in tubes so small that the two sides could be resolved only with difficulty with the magnifying power available.

A number 4 objective was used, the limitation imposed by the thickness of the wall of the Dewar preventing the use of one of higher magnifying power.

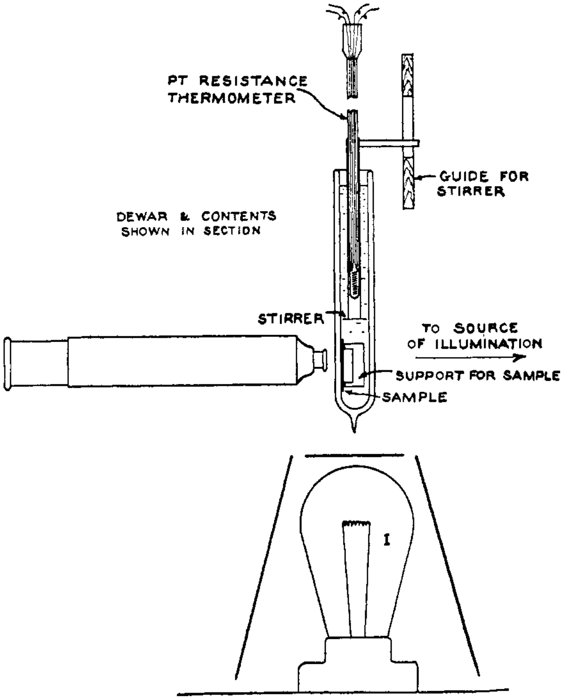

Fig. 3.

Determinations of critical temperatures were made on samples contained in two small capillary tubes whose internal diameters midway between the two ends were 0.004 and 0.060 mm., respectively, as measured microscopically and corrected for the magnifying power of the glass. Several determinations were also made on the 2-mm. tube shown in Fig. 1 and

Table I

Results of Experiments

	Tube no.		
	1	2	3
Internal diameter, mm.	0.004	0.060	2.0
Approximate length, mm.	15	15	80
Meniscus appeared	30.96 30.95	30.96	30.96
	30.985 30.94	30.96	30.96
Average	30.96	30.96	30.96
Meniscus disappeared	30.95 30.94	30.95 30.95	30.96
	30.98 30.93	30.96 30.96	
Average	30.95	30.955	30.96

these values are tabulated here for comparison. Temperatures are recorded at which the meniscus first appeared as the temperature was falling, and at the highest temperature at which a meniscus was seen as the tubes were slowly heated.

It will be observed that while the reproducibility of results on tube No. 1 leaves much to be desired, the average of the temperatures at which the meniscus appears is the same for all the tubes, that is, 30.96°. Similarly the meniscus disappears between 30.95 and 30.96°, taking average figures, for all of the tubes, regardless of size. Runs in which the temperatures changed more than 0.02° per minute are not tabulated above.

The temperature 30.96 ± 0.01° as the critical point of carbon dioxide, measured as here described, appears to be the most probable result, independent of the diameter of the tube in which it is measured. Whether the independence of capillary diameter and critical temperature holds in tubes whose diameter is of the same order of magnitude as the finest pores in charcoal or other adsorbing material, is of course conjectural. What is here proved is that there is no effect exceeding 0.03° for tubes as small as 4 microns in diameter.

The above figure is also suggested as an accurate value for the critical temperature of carbon dioxide, and the method here described as one of unexcelled precision, although more laborious than methods previously described. The greatest precision is probably attained in tubes the internal diameter of which is about 60 microns. The precision attainable in small tubes illuminated as described arises from the fact that up to the critical temperatures a sharp meniscus is observed. As the critical point is reached, violent motion is observed, and within a few thousandths of a degree, the meniscus, still moving, disappears. No bands or fog, such as are observed in large tubes with the naked eye, are visible.

Comparing the value here reported with critical temperatures determined by the more recent investigators, it will be noted that the present value is, in general, low. Thus, Meyers and Van Dusen[6] set 31.1° as the best figure. Hein[7] obtained 30.97°; Cardoso and Bell,[8] 31.00°; Dorsman,[9] 31.10°; Bradley, Brown and Hale,[10] 31.26°; Onnes and Fabius,[11] 30.985°; Brinkmann,[12] 31.12°; Keesom[13] 30.98°, and von Wesendonck[14] considered

---

[7] Hein, *Z. physik. Chem.*, **86**, 385 (1913–1914).

[8] Cardoso and Bell, *J. Phys. Chem.*, **10**, 500 (1912).

[9] Dorsman, "Dissertation," Amsterdam, **1908.**

[10] Bradley, Brown, and Hale, *Phys. Rev.*, **26**, 470 (1908).

[11] Onnes and Fabius, *Verslag. Akad. Wetenschappen Amsterdam*, 44 (1907); *Comm. Phys. Lab. Univ. Leiden*, No. 98, **1907.**

[12] Brinkmann, "Dissertation," Amsterdam, **1904.**

[13] Keesom, *Verslag. Akad. Wetenschappen Amsterdam*, 321, 533, 616 (1903); *Comm. Phys. Lab. Univ. Leiden*, No. 88, **1903.**

[14] Von Wesendonck, *Verh. deutsch. phys. Ges.*, **5**, 238 (1903).

the critical temperature indefinite within the range 30.95 to 31.7°. Among the results obtained previous to 1900, Andrews' value[15] of 30.92° is the lowest, all other temperatures recorded being 31.0° or higher.

The critical temperature, as used in this work, is the highest temperature at which a meniscus of sufficient sharpness to be seen in the field of a microscope when the material is examined by transmitted light can be observed. As the same results were obtained with an ordinary reading glass as with the microscope previously described, it is believed that this definition need not be amplified as regards magnification. It is suggested that the variation in critical temperatures as measured by the more modern workers in this field is due largely to the different criteria employed to define the critical point. Thus, when the 3-mm. tube used by Meyers and Van Dusen was examined by the author using transmitted light of high intensity[16] no meniscus that was entirely sharp was observed above 30.97°. By reflected light, however, a wide band was observed up to 31.1°, and fog at temperatures above 31.11°. Similarly, when the tube shown in Fig. 1 was observed by reflected light, a wide band was observed up to 31.04°. Observations on the band could not be repeated with satisfactory precision.

The selection of any one of the various physical phenomena which occur at the critical temperature as a means of defining this temperature precisely is necessarily somewhat arbitrary. Of the two phenomena described in this paper, namely, the appearance or disappearance of a band and the appearance or disappearance of the meniscus, the latter seems to be better adapted for practical definition of the critical temperature. It has been pointed out by Mr. C. H. Meyers,[17] however, that, due to the extreme compressibility of a substance in the critical region, a pressure gradient such as that due to gravity may cause a region of rapidly changing refractive index in a single-phase system, giving the appearance of a band which becomes sharper the nearer the temperature approaches the critical, as here defined.

This opportunity is taken to acknowledge with gratitude the encouragement and advice received from Dr. J. C. W. Frazer and Dr. W. A. Patrick, of the Department of Chemistry, Johns Hopkins University, whose guidance has made this work possible.

The kindness of Dr. H. C. Dickinson, Chief of the Heat and Power Division, Bureau of Standards, in making available to the writer much of the apparatus and materials used in this work, is gratefully acknowledged.

---

[15] Andrews, *Trans. Roy. Soc. London*, II, **159**, 575 (1869).

[16] The tube used by Meyers and Van Dusen was mounted on a solid backed board and could not be illuminated from directly behind. The meniscus was observed by so placing a 200-watt tungsten lamp that the line between the lamp and the observer's eye was nearly parallel to the board.

[17] Private communication.

To Mr. C. H. Meyers of the Bureau of Standards, especial credit is due for placing at the writer's disposal his specialized knowledge of critical temperature determinations, and for assistance freely given in cases where two observers were required.

Summary

The critical temperature of carbon dioxide has been measured in glass tubes ranging from 2 mm. to 0.004 mm. in diameter. The critical temperature was found to be independent of the size of the tube and 30.96° was taken as the most probable value. Large differences in critical point were found for different methods of illumination and depending on whether a sharp meniscus or diffuse band is taken as a criterion.

BALTIMORE, MARYLAND

[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 194]

VOLUMETRIC DETERMINATION OF VANADIUM BY MEANS OF POTASSIUM IODATE

BY ERNEST H. SWIFT AND RAYMOND W. HOEPPEL

RECEIVED NOVEMBER 13, 1928 PUBLISHED MAY 6, 1929

Introduction

The advantages of the iodate method of volumetric analysis have been pointed out by Andrews[1] and Jamieson,[2] and more recently reviewed by Heisig.[3] Among these advantages are the ease with which a standard solution of potassium iodate is prepared and the stability of its solution. Not only can substances which reduce iodate in hydrochloric acid solution be titrated, but it has been shown by Andrews[1] that oxidizing agents, such as chromates and chlorates, which oxidize iodide and are not re-oxidized by iodine monochloride, can be determined by adding an excess of a standard solution of potassium iodide and then converting the iodine liberated and the excess of iodide to iodine monochloride by titration with iodate solution. It was to be expected that a similar determination of vanadium as vanadate could be made, provided a sufficiently high concentration of hydrochloric acid could be maintained during the titration with the iodate to prevent re-oxidation of the quadrivalent vanadium formed. The chemical reactions involved in such a process can be represented as follows

$$H_3VO_4 + HI + 2HCl = VOCl_2 + \tfrac{1}{2}I_2 + 3H_2O$$
$$2I_2 + HIO_3 + 5HCl = 5ICl + 3H_2O \text{ and}$$
$$2HI + HIO_3 + 3HCl = 3ICl + 3H_2O$$

---

[1] Andrews, *Z. anorg. Chem.*, **36**, 83 (1903); THIS JOURNAL, **25**, 756 (1903).

[2] Jamieson, "Volumetric Iodate Methods," Chemical Catalog Co., New York, **1926**, p. 9.

[3] Heisig, THIS JOURNAL, **50**, 1687 (1928).