found that the solubility of metallic sodium in molten sodium chloride is 15 to 20% at 850° and increases with increasing temperature; moreover, the color of the solutions was reddish-brown. No silver chloride was found when the polarographic melt was dissolved in water, so that reduction of the alkali metal chloride was not caused by silver metal. It appears that sodium chloride was electrolyzed even at very low applied potentials to yield metallic sodium. No gas evolution was observed at the anode. The electrolysis current was large, making polarography for trace constituents in such a solution impossible.

A dropping silver electrode in a borax melt gave a much lower background current, but little could be obtained from the erratic polarograms because of the rapid attack on the quartz capillary by the melt.

Acknowledgments.—The authors wish to acknowledge the helpful advice of Drs. O. J. Kleppa, T. Rosenqvist and W. M. Saltman, and Mr. R. E. Fryxell of this laboratory.

Summary

1. Typical polarographic waves have been obtained for the reduction of a number of cations at the dropping mercury electrode in a melt of lithium, sodium, and potassium nitrates.

2. The Ilkovic equation has been found to apply for the reduction of the divalent ions of nickel, lead, cadmium, and zinc in the ternary nitrate melt at 160°.

3. The theory of the current–voltage relation has been experimentally confirmed in the nitrate melt for the cations mentioned above. Half wave potentials calculated from experimentally determined amalgam potentials for lead, cadmium, and zinc were in good agreement with the observed values.

4. Dropping lead and cadmium amalgam electrodes in the nitrate melt yielded anodic waves whose half wave potentials agreed with those for the reduction waves of the corresponding ions. Diffusion coefficients for lead and cadmium in mercury at 160° were calculated fromthe Ilkovic equation by the use of the anodic diffusion currents obtained with dropping amalgam electrodes.

5. Attempts to operate dropping electrodes of pure lead and bismuth in a molten lithium chloride–potassium chloride melt were unsuccessful. Dropping molten silver electrodes gave no useful polarograms in sodium chloride or borax at 1000°.

RECEIVED JANUARY 9, 1950

[CONTRIBUTION FROM THE CRYOGENIC LABORATORY AND THE DEPARTMENT OF CHEMISTRY, THE OHIO STATE UNIVERSITY]

The Direct Determination of the Critical Temperature and Critical Pressure of Normal Hydrogen[1]

BY DAVID WHITE, ABRAHAM SOLOMON FRIEDMAN AND HERRICK L. JOHNSTON

Introduction

The earliest determinations of the critical pressure and critical temperature of hydrogen were made by Olszewski[2,3] who first reported the critical pressure as 20 atmospheres and the critical temperature as −234.5°, but later gave them as 13.4 to 15.0 atmospheres and as −240.8°, respectively. Dewar[4,5,6] obtained values ranging from 15.0 to 19.4 atmospheres and from −221 to −243°. Bulle[7] obtained values of 11.0 atmospheres and −241.15°, respectively. Although he used a direct method, his data suffered from the presence of rather severe temperature gradients in his apparatus.

The values generally accepted today are those determined, indirectly, at Leiden[8] from extrapolation of PV isotherms in the neighborhood of the critical point, in conjunction with the vapor pressure curve. Their values of the critical pressure and temperature are 12.80 atmospheres and −239.92°,[9] respectively. A complete summary of the investigations on critical phenomena for hydrogen has been given by Pickering.[10]

We have designed and constructed an apparatus for accurate direct measurements of critical temperature and pressure. This work has seemed worthwhile because of the need for accurate values of the critical constants in correlating reduced equations of state for pure gases and gaseous mixtures[11] with such molecular properties as intermolecular potentials and collision diameters. Additional interest in critical phenomena has been aroused by theories of condensation in the critical region recently advanced by Mayer[12] and by Rice.[13] Our first data, with the new apparatus, has been taken on hydrogen.

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[1] This work was supported in part by the Air Materiel Command under Contract with The Ohio State University.

[2] K. Olszewski, *Phil. Mag.*, **39**, 202 (1895).

[3] K. Olszewski, *Ann. Physik*, **7**, 986 (1905); **8**, 193 (1906).

[4] J. Dewar, *Proc. Roy. Soc.* (*London*), **64**, 227 (1899).

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[6] J. Dewar (reported by Clerke), *J. Phys.*, **4**, 1, 116 (1902).

[7] F. Bulle, *Physik. Z.*, **14**, 86 (1913).

[8] K. Onnes, C. A. Crommelin and P. G. Cath, *Leiden Comm.*, **151C** (1917).

[9] In their determination, the ice point was taken to be 273.09°K. on the Leiden scale.

[10] S. F. Pickering, Bureau of Standards, Sci. Papers, No. 541, 597-629 (1926).

[11] W. B. Kay, *Ind. Eng. Chem.*, **28**, 1014 (1936).

[12] J. E. Mayer, "Statistical Mechanics," John Wiley and Sons, Inc., New York, N. Y., 1940.

[13] O. K. Rice, *J. Chem. Phys.*, **15**, 3141 (1947).

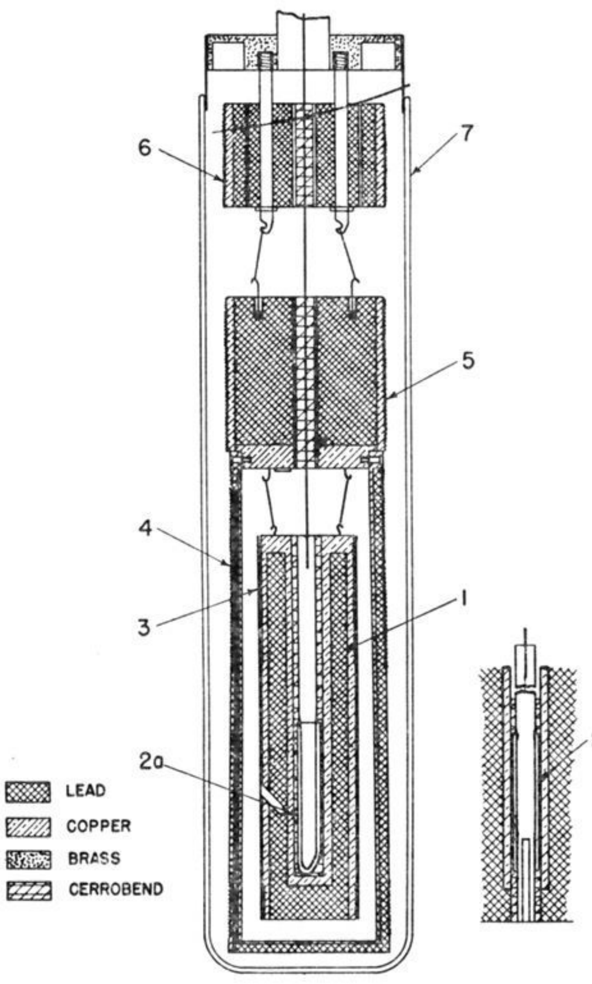

Fig. 1.

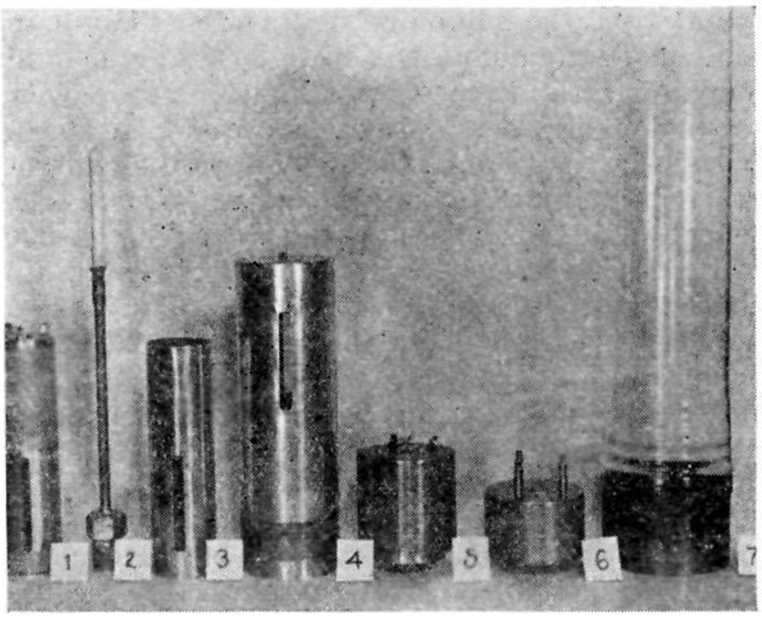

Fig. 2.

Apparatus.—The apparatus (Figs. 1 and 2) is basically similar to the vacuum calorimeter construction widely used in the design of low temperature apparatus in this Laboratory.

The liquid whose meniscus is under observation is condensed in a section of glass capillary (2)[14] that communicates, through a 0.025-inch o. d. stainless steel capillary soldered into the copper portion of a glass-to-copper seal,[15] with a heavy walled glass U-manometer, a source of pure hydrogen, and an M. I. T. type dead-weight gage. This glass capillary, which with its glass-to-metal seal can withstand a pressure of 65 atmospheres, is embedded in Cerrobend inside of a lead-filled copper pipet (1). The pipet is surrounded by a gold-plated copper radiation shield (3) and a lead-filled copper "lower block" (4). Each of these surrounding cylinders is provided with longitudinal slots through which the glass capillary can be observed. The "lower block" is attached to a lead-filled copper "upper block" (5), from which the copper pipet (1) and radiation shield (3) are also suspended. The "upper block" (5) in turn, is suspended by nylon strings from a lead "auxiliary block" (6), which is suspended by monel lugs from the under side of the vacuum-tight brass lid of the surrounding "container" (7). The container is, effectively, a large glass test-tube, 75 cm. in diameter, having a glass-to-metal seal at its upper end. The glass "container" is coated with aluminum paint except where longitudinal slits are provided for observation of the meniscus in the glass capillary.

The purpose of the "blocks" is to trap off heat leak down the thermocouple, the stainless steel capillary, and the heater wires. Wires that pass through the blocks are embedded in paraffin, and the stainless steel capillary in Cerrobend alloy.

The temperature of the glass capillary is taken to be that of the copper pipet (1), whose temperature was measured to a precision of 0.005° by means of a copper–constantan thermocouple whose junction, embedded in Cerrobend, is inserted in a well in the pipet. The pressure of gas or vapor in the capillary is measured by means of the dead-weight gage, which has a precision of 1 part in 30,000 at 25 atmospheres.

For the measurements on hydrogen, the vacuum-tight container was suspended in a bath of liquid hydrogen boiling at atmospheric pressure.

Modified Apparatus.—Because it was recognized that there might be a small temperature difference between the copper pipet and the liquid hydrogen on the inside of the glass capillary, a second glass capillary was prepared with glass-to-copper seals on both the upper and lower ends (insert 2b of Fig. 1). The standard thermocouple was then embedded in a copper thermocouple well that projected through a soldered joint, in the copper portion of the lower seal, into the liquid hydrogen at the bottom of the glass capillary.

Data were taken with both forms of apparatus. The modified form always gave slightly lower readings than the earlier form; however, the difference in readings never exceeded 0.01°.

Experimental Procedure.—When exchange gas was introduced into the vacuum-tight container, enough normal hydrogen was condensed in the glass capillary, at a temperature about 1° below the critical point, to bring the meniscus about halfway up the capillary. The exchange gas was pumped out until a vacuum of better than 10^{-3} mm. was obtained; the blocks were next heated to a temperature slightly above the critical point to be certain that no liquid existed in the stainless steel capillary; the temperature was then raised by increments of a few hundredths of a degree, while the meniscus was observed.

When the meniscus exhibited marked flattening, the pressure was read on the dead-weight gage, and the system was then shut off from the gage, to reduce the total volume of the system. The glass capillary manometer was then employed to read further pressure increments while the small heating increments were continued. Twenty to thirty minutes were allowed after each heating period to permit attainment of thermal equilibrium. The temperature and pressure at which the meniscus disappeared were carefully noted. In one run, with the second capillary, the critical point was approached from the higher as well as the lower temperature side. The approach from the higher side was accomplished by admitting a small quantity of exchange gas to the vacuum space and by observing the temperature and pressure readings when the meniscus reappeared.

The equilibrium readings of temperature and pressure obtained during the approach to the critical point con-

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[14] The numbers in parentheses refer to the numbering of parts in Figs. 1 and 2.

[15] The heavy tube and the hexagonal fitting shown in Fig. 2 is not the thin capillary referred to, but is a section of thicker tubing used in calibration.

stitute vapor pressure points for the liquid just under the critical temperature.

Experimental Results

After preliminary runs to develop techniques of measurement, one series of data runs was made with the first capillary and three series with the second capillary shown in insert 2b Fig. 1. Each series was made with a fresh filling of purified hydrogen.

Table I is a record of the equilibrium data obtained on the first of these four series of runs and Table II a record of the the second series.

TABLE I

VAPOR PRESSURE OF NORMAL HYDROGEN IN THE NEIGHBORHOOD OF THE CRITICAL POINT (OBSERVATION OF CRITICAL DATA)

Series of runs with the first glass capillary

Temp., °K.	Pressure, atm.	Remarks
33.08	12.525	Meniscus flat
33.10	12.530	Meniscus flat
33.14	12.625	Meniscus faint
33.21	12.714	Meniscus faint
33.23	12.733	Meniscus very faint
33.25	12.783	Meniscus disappeared

Critical temp. and press. 33.25 °K. and 12.783 atm.

TABLE II

VAPOR PRESSURE OF NORMAL HYDROGEN IN THE NEIGHBORHOOD OF THE CRITICAL POINT (OBSERVATION OF CRITICAL DATA)

Series of runs with the second glass capillary

Temp., °K.	Pressure, atm.	Remarks
33.14	12.615	Faint, flat meniscus
33.15	12.620	Faint, flat meniscus
33.22	12.742	Faint, flat meniscus
33.25	12.808	Meniscus disappeared

Critical temp. and press. 33.25 °K. and 12.808 atm.

Table III is a tabulation of critical data obtained in all four data series, including the data obtained by approach from higher temperature.

TABLE III

SUMMARY OF OUR OBSERVATIONS OF CRITICAL CONSTANT FOR NORMAL HYDROGEN

Data series	Capillary	Approach	Critical temp., °K.	Critical press., atm.
1	First	Rising	33.25	12.783
2	Second	Rising	33.25	12.808
3	Second	Rising	33.24	12.804
4	Second	Rising	33.24	12.802
3	Second	Falling	33.24	12.790
		Averages	33.244	12.797

Observations made during the three series of runs with the second capillary always showed that the temperature of the liquid hydrogen in the capillary was slightly lower than that of the copper pipet, but the difference never exceeded 0.01°. Accordingly, we have used the observation made with the first capillary without correction.

Discussion

The vapor pressure data given in Tables I and II are plotted in Fig. 3. They agree well with those obtained in a separate investigation with a different apparatus.[16]

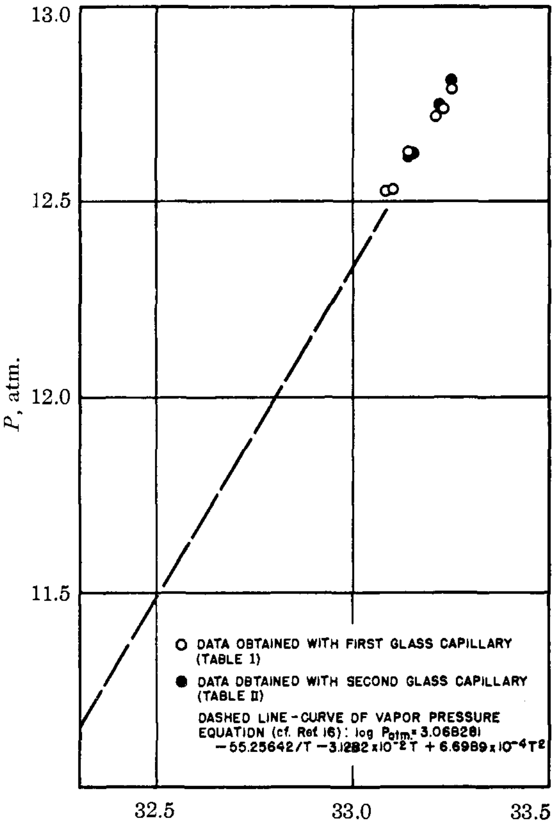

Fig. 3.

The critical temperature observed in this direct research, 33.244° K., also agrees well with that computed from our earlier vapor pressure equation, 33.25°K., when P is set equal to 12.797 atm. The consistency between these independent sets of data indicates that equilibrium was reached in our glass capillaries.

Our laboratory temperature scale, on which our assignment of critical temperature depends, is believed accurate to within ±0.02° in this region of temperature. Our temperature scale will be discussed in separate papers from this Laboratory.

The conversion of ortho to para hydrogen during the run was, at most,[16] only 2 or 3%, since the longest period during which a sample of liquid was kept in the capillary was six hours, the usual period being approximately an hour.

It is interesting to note that no opalescence was observed in the neighborhood of the critical temperature in either heating or cooling. An attempt was made to bring on the opalescence by shaking

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[16] D. White, A. S. Friedman and H. L. Johnston, THIS JOURNAL, **72**, in press (1950).

the pipet. Since the pipet was suspended by means of nylon strings, it was possible to shake the liquid. In fact, a few times it was observed that the meniscus splattered on shaking, however, no visible opalescence occurred. The only conditions under which one could obtain momentary opalescence was by cooling the system rapidly. The opalescence persisted for only a few seconds after cooling was stopped.

From Mayer's[12] and Rice's[13] theories of liquids in the critical region, one would expect opalescence to occur due to differences in density at the critical point. Failure to observe opalescence, therefore, indicates either that the theories are incorrect or that the density differences are particularly small for hydrogen.

It is interesting to note that our own direct measurements of critical pressure and of critical temperature are in close agreement with those computed at Leiden,[8] from data of state. Values of critical temperature differ by only 0.07°. Since the Leiden data were obtained from the *P–V* isotherm for which a flat portion occurs (as well as from the vapor pressure data), it appears that, in the case of hydrogen, no flat portions exist above the critical or that the temperature range over which they do exist is extremely small. The former description would contradict the Mayer theory, but is consistent with the Rice theory which does not postulate isotherms with flat portions above the observed critical temperature and pressure. This subject will be further investigated in connection with the high pressure *P–V–T* program now under way in this Laboratory for a number of gases and liquids.

Acknowledgment.—We wish to acknowledge the helpful suggestions of Mr. L. E. Cox, Shop Foreman of the Cryogenic Laboratory, in the design and construction of the apparatus.

Summary

A new apparatus has been constructed to measure accurately and directly critical constants of condensed gases. The critical constants of normal hydrogen have been determined and found to be 33.24$_4$°K. and 12.797 atmospheres. The vapor pressure of normal hydrogen in the immediate vicinity of the critical temperature has also been measured.

COLUMBUS, OHIO RECEIVED FEBRUARY 3, 1950

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE ILLINOIS INSTITUTE OF TECHNOLOGY]

The Kinetics of the Zirconium–Nitrogen Reaction at High Temperatures

BY ANDREW DRAVNIEKS[1]

Introduction

Zirconium is known to react with most gases.[2–5] Nitrogen is taken up in a solid solution with only slight expansion of the zirconium lattice. Under suitable conditions a thin nitride film is also formed on the surface of the metal phase.[6] Hayes and Roberson[6] measured the hardening of the metal caused by nitrogen in solid solution. Recently Gulbransen and Andrew[7] investigated the kinetics of the nitrogen uptake by zirconium at temperatures up to 850°, and observed no film formation under conditions employed.

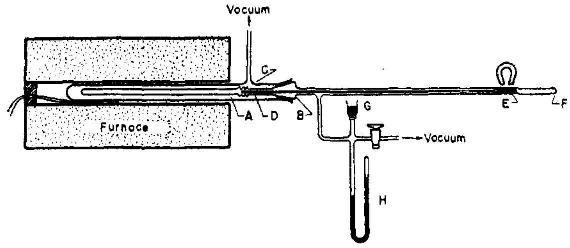

Fig. 1.—Apparatus for measuring gas–metal reaction rates.

In the present work a kinetic study has been made of the zirconium–nitrogen reaction at higher temperatures where a well-defined zirconium nitride phase is formed in addition to a solution of nitrogen in zirconium metal.

Experimental

The rate of the nitrogen–zirconium reaction was measured by observing the pressure decrease in the apparatus shown schematically in Fig. 1. A silica glass tube A, containing the specimen, was connected by a graded seal to a Pyrex ground joint B and inserted into a continuously evacuated silica glass jacket C. The vacuum jacket prevented the passage of air through the silica and, hence, kept the nitrogen atmosphere in the inner tube free of oxygen at temperatures up to 1050°. The specimen D was hooked on the end of a silica glass rod supplied with a sealed-in iron rod E. The rod and specimen were introduced through the end of the glass tube F which was then sealed. With the specimen in the cold part of tube A, the system was evacuated to 10^{-6} mm., then nitrogen was introduced by immersing a capillary, through which the gas was flowing, so as to touch the porous glass plate under the mercury seal G. The pressure in the system was read on mercury manometer H to ±0.05 mm. with a cathetometer.

A strong current of air was blown by an electric fan on the parts of apparatus outside the furnace; temperature readings of the air were taken in order to correct for the small changes in room temperature. To start a run, a specimen was pushed by means of a magnet into the hot zone and pressure measurements begun.

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