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THE THERMODYNAMIC PROPERTIES OF METHANE

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1 Introduction The Vapor Pressure of Methane. There are very few published data for the vapor pressure of liquid methane. Olszewski's¹ results extend from the critical temperature to the freezing point, but the pressures are several atmospheres greater than the recent measurements of Cardoso² in the interval -84.4° to -97.0° . The critical pressure, for example, obtained by Olszewski is 54.9 atms at a critical temperature given as -81.8° whereas Cardoso gives 45.60 atms at -82.85° . No other measurements have been found in the literature.

In the case of methane there are two very material difficulties connected with securing accurate vapor pressure values. Thus it is necessary to maintain and measure temperatures from -80° to -180° and insure that the temperature readings lie on the absolute scale of temperature. The latter objective is by no means easy to insure, since the comparisons of secondary standard thermometers with the gas scale have not reached a stage where satisfactory concordance has been attained between various investigators. The relation of the platinum resistance thermometer to the gas scale, for example, has been shown by Henning³ not to be the same below zero as above zero where the Callendar formula applies. In fact, no two of Henning's eight platinum resistance thermometers appeared to give identical readings at all temperatures below zero, although the δ constants of Callendar, obtained by using 0° , 100° , and 419.4° for some of the thermometers, were almost identical. The general inference was that the differences between the gas scale and the Callendar formula temperatures of the platinum resistance thermometers were very markedly affected by small variations in the temperature coefficient of the platinum wire.

¹ Olszewski, C. r. **100**, 940, 1885

² Cardoso, Jour. de Chim. et Phys. **13**, 332, 1915

³ Henning, Ann. d. Phys. **40**, 635, 1913

The further need in accurate low temperature work is a constant temperature bath whose temperature can be changed at will from zero to the lowest temperatures required. The use of liquids boiling under constant pressure for this purpose has been highly developed in the Leiden cryogenic laboratory of Professor Onnes, but is not as convenient as desirable owing to the necessity of changing the bath liquids for studies covering long temperature ranges. It is, in addition, necessary to vary and maintain constant the pressure over the boiling liquids. The device used by Henning in the paper referred to above consisted of a test tube, submerged in a bath of petroleum ether, into which liquid air is dropped as required. Evidently a bath of this description would be troublesome to use where observations are to be made requiring concentration of attention on the details of the physical measurements.

The purity of the methane to be used is of paramount importance. For the present work samples of the methane were employed prepared as described in the preceding paper on the equation of state of methane.

In view of the uncertain status of the behavior of the platinum resistance thermometer at low temperatures an investigation had already been made in the physics department laboratories of this Institute of the relation between the scales of the platinum resistance thermometers actually used in the present investigations with the gas scale. The freezing points of a number of substances lying between zero and the boiling point of oxygen were also measured in terms of the constant volume hydrogen gas scale to serve as calibration temperatures.

The question of the thermodynamic scale is of particular importance at low temperatures, since the effect of a given error in temperature measurements is of increasing significance as lower temperatures are approached. Thus for example, 0.1° at the ice point, 273.14, is an error somewhat greater than 1 per 3,000, whereas 0.1° at the boiling point of oxygen, 90.20, is of more than three times this magnitude. The temperatures recorded in the present paper are, then, those obtained by means of a platinum resistance thermometer compared directly with the constant volume hydrogen thermometer at a number of temperatures between zero and the normal boiling point of oxygen.

2 Apparatus Details. The apparatus of first importance is the cryostat represented to scale in Fig 1. It consists of two pyrex Dewar tubes, one of which A serves to contain liquid air, or, under certain conditions, liquid ammonia. Support for the larger tube is provided by means of a brass ring encircling the flask and attached thereto are three brass strips screwed to the cast-iron

Fig. 1

base S. The cast-iron base also serves to carry the support rod for the motor H used to stir the contents of the bath itself. The inner Dewar tube is supported in the larger tube by means of an asbestos wood cover into which the smaller tube is cemented. The inner Dewar tube is provided with a cork support at its tip, from which a tube V leads to a source of hydrogen or to a vacuum.

The outer tube is silvered except for a rectangular strip which permits a view of the interior. The inner Dewar tube is supplied with a cover which serves as a support for the stirrer, heater, temperature regulator and platinum resistance thermometer. The cover of hard rubber is held firmly in place by three bolts carrying tongues of brass which fit into a slot turned into the periphery of the hard rubber cover. An opening is also provided at J for the introduction of the apparatus upon whose contents observations are to be made. It is, of course, essential that the introduction of heat by conduction should be a minimum and for this reason the stirrer rod C is interrupted by a hard rubber connector just under the cover. The shank of the thermometer is of monel metal turned to about 0.2 mm thickness, and having the silver sheath containing the platinum wire silver-soldered thereto. The regulator consists of a 3 mm width and 0.75 mm thickness invar-brass thermostat metal*. This is wound in a helix as indicated and the upper end soldered to a thin brass tube. The lower end carries, floating, a fine monel rod passing loosely through a hard rubber bushing shown shaded at G. Here two platinum contacts are arranged and as the helix winds and unwinds, due to temperature changes, contact is made and broken. The sensitivity is limited by the pressure necessary to make electrical contact. The maximum sensitiveness which has thus far been attained at the lower temperatures is about 0.1° . The platinum resistance thermometer, however, indicating 0.001° makes it easy to secure a temperature constant to 0.01° . The combination of hand regulation with the automatic requires an operator to watch the galvanometer of the resistance bridge and manipulate resistances in accordance with the deflections of the galvanometer. The bimetallic helix, on the other hand, would have great sensitivity were it not for the really considerable pressure needed for good electrical contact. It is hoped that in time means for surmounting the latter difficulty will be evolved, since it is most convenient to have the bath automatically regulated.

The heater consists of a very thin steel, or preferably monel, tube upon which is wound the resistance wire over thin mica.

* This excellent material was obtained in several thicknesses and lengths through the kindness of the H. A. Wilson Co. of Newark, N. J.

Fig. 2

Talc plugs serve to insulate the free end of the wire which passes through the center of the supporting tube

The method of operating the bath consists in adjusting the pressure of hydrogen in the interspace of the Dewar tube B until sufficient cooling of the bath fluid is secured to balance the mean value of the heating current. For the lowest temperatures, for example, as good as possible conductivity of the interspace is required and a centimeter pressure of hydrogen is sufficient. At high temperatures, on the other hand, a relatively low pressure is necessary on account of the greater difference in temperature between the contents of the cryostat bath B and the surrounding liquid air. For temperatures above -30° it is best to use liquid ammonia in the outer dewar tube, and thus any temperature in the range between 0° and -180° may be easily established and maintained.

The vapor pressures were measured in two separate pieces of apparatus. Pressures above several atmospheres were measured at the time the densities of the liquid were being measured, while a special apparatus was used for the lower pressures down to the triple point. In Fig. 2 is represented the block C as described in the preceding paper on the equation of state for methane. A is the mercury oil contact, the oil lead connecting with the piston pressure gauge. C leads to the mercury volume-measuring injector and B leads to the vacuum pump. The electrical circuit for indicating mercury contact at the oil junction within A consists of an audion bulb, induction coil primary, dry batteries and telephone.

The steel stopcock D serves to shut off the mercury in the pyrex glass volume-measuring apparatus* E, which connects by

*The coefficient of temperature expansion of pyrex glass has not been measured at low temperatures. The following equation for the true volume at any temperature t is based on the mean expansion measurements in a weight-thermometer of pyrex glass between 0 and 100, and 100 and 218°

$$V_t^{\text{pyrex glass}} = V_o (1 + 9.68 \times 10^{-6} t + 3.11 \times 10^{-9} t^2)$$

The error that extrapolation to -180° may introduce in the measurements of the specific volume of liquid methane is inconsiderable unless the coefficient of expansion of pyrex glass is widely different from soda glass in its general expansion behavior. This is not inferred since its expansion properties are quite similar to soda and other glasses above zero.

The expansion of the volumometer with pressure was determined at zero degrees by blank measurements with the bell F sealed off from the

0.75 mm bore pyrex glass tubing at one side with the steel cock** D and at the other with the pyrex glass bell (2.75 cm diameter and 12.5 cm long) enclosed in the steel case F. The capillary lead L is used to exhaust the glass portion previous to the introduction of the methane. The compressor G connecting with F serves to force methane into E where the liquid volumes were measured. It is perceived that the apparatus consists of a constant volume portion E, which can be filled with liquid methane at any temperature in the liquid region by manipulating the mercury injector G transferring methane from the reservoir F at ordinary temperatures.

The volume of E (1.5798 c.c. at 0°) together with the capillary leads was determined by filling with mercury and weighing. The volume of the bell within F (about 75 c.c.) was measured by means of the piston G. The injector G (total volume capacity 56 c.c.) was calibrated by weighing the mercury ejected for each five turns of the nut advancing the piston. The position of the piston was indicated by a "cyclometer" giving the number of whole turns, and the fractions of a turn, on the nut whose periphery was divided into one hundred divisions. The piston was so adjusted that practically at its maximum inward travel the mercury stood at a mark on the capillary of determined volume per unit length above F. The glass bell was, of course, so

volumenometer. Correction could, therefore, be made for the stretch of E with pressure although this was not determined as a function of the temperature. Previous experience with soda glass above zero has shown that the temperature coefficient of the pressure stretch is very small within the elastic limits of the glass.

**In Fig. 2a is represented an enlarged drawing of the method employed to connect the steel and glass. The glass capillary F is thickened to an inverted cone shape and ground to fit the steel piece D. The member D is then warmed and a thin layer of a cement made from shellac which has been digested on a water-bath with fifteen per cent of North Carolina oil of tar, is wiped over the ground surface. The glass member is now seated in the steel part D, turning the glass member in its seating position until the cement is squeezed out and the ground surfaces in as close contact as possible. Connection can now be made with any other part of the steel apparatus, as represented at A, by means of a union B, using an annealed aluminum disk C. The glass capillary F should be joined *in situ* to the remaining portion of the glass apparatus to avoid strains at the rigid steel construction. The joint of the steel and glass bell F is made in the same manner as described. The joints described are vacuum tight, resist the action of mercury and hold against pressure to the limit of the glass. They cannot be used, however, above 100°.

proportioned (75 c c capacity) that when the piston was withdrawn to the complete outward travel of the screw, mercury sealed the lower end of the bell. Methane from the storage globe was now passed over into a measuring burette, similar to the one used in loading the piezometer employed in measuring the isometrics of the gas phase, and condensed finally in E at the temperature of liquid oxygen. The capillary lead at L was then sealed and the gas remaining in the leads between L and the measuring burette pumped off and measured. Before E was allowed to warm to room temperature the mercury was lowered in F to the maximum by withdrawing the piston of G. The methane could then be safely allowed to evaporate from E, filling a space of about 56 c c and producing a total pressure of only 10 atms at ordinary temperatures.

To make a measurement of the specific volume the volumenometer E was brought into the cryostat already described. A glass scale divided into millimeters was placed back of the volumenometer serving to give indication of the position of the level of the meniscus of liquid methane relative to two etched marks on the capillary extensions from the volumenometer bulb. At a fixed temperature mercury was forced over from a second mercury injector communicating from B until the meniscus was just about at the level of the cover of the cryostat and fixed in position by closing the steel stopcock D. By means of G methane was forced to condense in E until the liquid methane menisci were about at the two etched marks on the volumenometer stems. A fixed volume of liquid methane was, therefore, confined by the gas phase present in the capillary leads. The total mass of methane was known after sealing at L and the volume, temperature and pressure of the methane existing in the gas phase, from the reading of the position of the piston of the injector G and the volume of the glass capillary tubing. By means of the equation of state the mass of this known total gaseous volume could be computed, and the mass of the liquid methane of known volume in E deduced. Before changing the temperature of the cryostat the steel cock D could be opened and an observation made of the vapor pressure. In this manner practically the whole temperature range of the existence of the liquid phase could be measured. The critical temperature was ascertained and also the critical pressure.

In the procedure described no mention has been made of the influence of adsorption in removing methane from the phase under observation. The volumenometer E was exhausted at 360° for several hours previous to admitting the methane. No certainty is afforded that adsorption did not take place, but freeing the glass surface from adsorbed moisture appears, from general experience, to minimize the adsorption of the permanent gases*. The bell F could not be evacuated hot, so that no certain knowledge is available as to the amount of methane adsorbed. The total

Fig. 3

mass of methane was, however, sufficiently large, so that, if ten molecular layers of methane were adsorbed, the effect would scarcely be detectable with the accuracy attainable in the volumenometer measurements.

The measurements of saturation pressure below several atmos-

* It was shown by Eumorphopoulos (Proc Roy Sci **90** A, 189, 1914) that only by repeatedly heating and rinsing with dry nitrogen could the coefficient of volume increase with temperature at constant pressure be made reproducible. Isometric measurements with ammonia in this laboratory have indicated that adsorption is greatly minimized by long baking out of the glass at the best vacuum obtainable.

pheres were carried out in a special apparatus, since the piston gauge is not suitable for low-pressure measurements. The general apparatus is represented in Fig. 3. The manometer tubes were selected of uniform bore, 1.5 cm. in outside diameter and the actual diameter along the length determined by weighing mercury taken from successive intervals along the length of the longer leg. The short leg of the manometer was provided with a finely pointed platinum wire sealed into the closed end and the diameter accurately determined at the section in the plane of the point. With the true tube diameters a table was then computed giving the correction for capillary depression for different heights of mercury. The corrections for capillary depression with tubing 1.5 cm. I.D. will rarely exceed a few hundredths mm. with tubes of moderate uniformity of bore. Each manometer tube was ground to a seat in the steel block A* having steel cocks to cut off the two legs of the manometer and the levelling reservoir E. The mercury in the reservoir E was passed through the trap D to prevent air from gaining access to the manometer tubes, and all connections were of glass. Compressed air and vacuum served to manipulate the entrance and exit of mercury to the manometer, while fine adjustment was secured by means of the mercury piston injector C. The purpose of the platinum contact B in the short arm was to aid in observing equilibrium of the methane in the container F and to save continually reading the mercury level in the short arm, since the reading of the level when contact just makes is reproducible to the limit of sensitiveness of the cathetometer (0.02 mm.).

The methane container during the actual measurements consisted of the tube F containing an electro-magnetically operated glass stirrer as indicated. The coil G was energized periodically by means of the metronome contacting device represented. It

* The ground joints and block were warmed and set with the shellac cement, as described in the case of the steel-glass joint represented in Fig. 2. An enlarged and threaded portion was produced in the steel block above the ground cone, for the purpose of preventing the tubes floating off their seat. The tubes themselves were enlarged, as indicated, at a point where they would come within the threaded part and at the time of seating the tubes, when both glass and steel were hot, cement was poured into the threaded cavity. With the construction here indicated the glass cones can be made and ground so that the bore of the glass coincides with the communicating hole in the steel, eliminating thereby any tendency to trap gas.

is, of course, necessary to adjust the period of the metronome to the elastic characteristics of the spring by which the stirrer is suspended. The soft iron rod constituting the armature is enclosed in glass just below the eye used to fasten the lower end of the spring.

The exhaustion of the apparatus took place through the lead at L, while the long leg of the manometer was exhausted or exposed to the atmosphere at V depending on the magnitude of the pressure to be measured. The methane to be used in the measurements was transferred from the glass storage globes to the steel tube container M provided with a steel block carrying a cock and lead K. Methane was condensed in M by means of liquid air, after having been thoroughly exhausted. Connection was made to the glass apparatus by means of the shellac cement. When the entire apparatus was thoroughly exhausted to the cock in the steel block K, the tube F was brought into the cryostat, adjusted to the lowest temperature (-180°), and by opening the cock of the steel methane container, a quantity of methane was condensed in F for the measurement of the vapor pressure. The exhausting lead L carried a stopcock in order to permit of pumping the methane between successive measurements, thus insuring the absence of foreign gas, although the methane during its introduction into the container M was treated to remove all permanent gases. At the conclusion of a day's measurements, the methane could be transferred from the tube F to the container M and held under pressure for future measurements.

3 The Temperature Measurements. The temperatures recorded should lie on the absolute or thermodynamic scale and, while numerous investigations have resulted in fixing with considerable certainty the thermodynamic scale above zero, the temperature scale below zero, as already stated, is by no means as completely investigated. The difficulties, indeed, are increased in the region below zero, due to the difficulties of refrigeration, lack of convenient cryostats and errors introduced in the gas thermometry by adsorptive effects. The latter are of increasing significance as the temperature is lowered and are, moreover, par-

ticularly difficult to investigate quantitatively. Unfortunately, as Henning has shown, the platinum resistance thermometer does not follow the Callendar formula in its relation to the thermodynamic scale below zero. Moreover, owing to the fact that the wire contracts on cooling, it is not easy to devise a method of winding which will avoid the production of strains. Above zero, on the other hand, the wire expands and the tension of the wire on its support is relieved.

Owing to the importance of an accurate knowledge of the true temperature indications of the particular platinum thermometer employed in the present work, an extended comparison was made directly with the constant volume hydrogen thermometer employed in an investigation of the low temperature scale by Keyes, Townshend and Young in this Institute. The actual curve, (Fig 14 of their paper), shows the difference between the Callendar formula platinum resistance thermometer temperatures and those of the quartz hydrogen thermometer of constant volume. The hydrogen gas scale temperature of the boiling point of pure oxygen at 76 cm was found to be -182.94 as compared with -182.93 of Onnes⁴ and -182.97 of Henning⁵. The boiling point of carbon dioxide at 76 cm was similarly found to be -78.53 as compared with -78.52 found by Henning⁵.

4 The Vapor Pressure Measurements. The measurements at higher pressures made in the apparatus represented in Fig 2 extend from about 4.5 atms at 133.6° abs to the critical temperature 191.03° . The low pressure measurements extend from about 7.5 degrees above the triple point⁶ temperature to about 114.6° .

The higher-pressure measurements consist of two series presented in Table I. The low pressures were measured in a small cryostat whose diameter (6.7 cm) was small compared with the length (30 cm). Efficiency of stirring of the bath fluid of propane and butane is necessary before the experimental tube can be assumed to be at the same temperature as the thermometer.

⁴ Onnes and Braak, Leiden Comm. No. 107a, 1908.

⁵ Henning, *Ann. d. Phys.* **43**, 289, 1914.

⁶ Crommelin, *Com. Leiden Phys. Lab.* No. 131, 1912. The temperature of the triple point is given as -183.15 and the pressure 7.0 cm.

TABLE I
Methane Vapor Pressures

<i>Temperature Abs</i>	<i>Series 1</i>		<i>Temperature Abs</i>	<i>Series 2</i>	
	<i>Observed Pressure Atms</i>	<i>Calc Pressure Atms</i>		<i>Observed Pressure Atms</i>	<i>Calc Pressure Atms</i>
133 628	4 514	4 493	143 380	7 574	7 515
138 558	5 874	5 880	158 549	14 634	14 839
143 495	7 590	7 558	168 267	21 737	21 637
148 439	9 579	9 565	168 351	21 707	21 704
153 385	11 949	11 936	172 355	25 004	25 073
158 339	14 639	14 711	178 189	30 500	30 626
163 295	17 897	17 928	181 203	33 684	33 812
172 437	25 146	25 146	186 084	39 626	39 449
178 189	30 486	30 626	186 147	39 389	39 525
181 203	33 700	33 812	188 005	41 807	41 835
186 147	39 511	39 525	189 931	44 207	44 326
			191 031	46 063	45 792
			Crit		

TABLE II
Low Vapor Pressure Measurements of Methane

<i>T</i>	<i>Series 1 Pres- sures Atms</i>	<i>Series 2</i>	<i>Series 3</i>	<i>Series 4</i>	<i>Series 5</i>	<i>Series 6</i>	<i>Mean of Series 4, 5, 6</i>	<i>Pres- sure Calc by Equa- tion</i>
97 293	0 2638	0 2625	0 2620	0 2575	0 2575	0 2571	0 2574	0 2574
100 902	0 3855	0 3847	0 3815	0 3774	0 3785	0 3781	0 3780	0 3780
106 003	0 6276	0 6271	0 6228	0 6216	0 6210	0 6197	0 6208	0 6196
110 023	0 8925	0 8928	0 8858	0 8839	0 8852	0 8829	0 8840	0 8830
114 631	1 2917	1 2903	1 2860	1 2846		1 2812	1 2829	1 2823

Table II gives the low pressure series. The resistance bridge, in each series of measurements, made at different times, was brought to the same indication and the bath regulated at the corresponding temperature. In this manner the various changes in the external conditions affecting the measurements could be investigated. It was found necessary to increase the speed of the stirring of the bath markedly to secure constancy of the vapor pressure and also the agitation of the liquid methane by means of the electro-magnetic stirrer. To establish the absence of hydro-

gen or air the vapor phase of the methane could be pumped off from time to time during the measurements, and at the conclusion of the day's run from the frozen methane in the steel container before closing the steel cock K. The three final series 4, 5, and 6 show equilibrium was attained and these values have been used to form the mean pressure upon which the equation for the vapor pressure as a function of the temperature was based.

Some disappointment was felt that the measurements at higher pressures presented in Table 1 were not more concordant. This is not due to any lack of sensitiveness in the pressure-measuring device or lack of constancy in the temperature of the cryostat. It is believed to be due possibly to lack of sufficient stirring or agitation of the liquid methane under measurement. The construction of the apparatus and the purpose it had to serve precluded an effective stirring device, but a form of stirrer is being perfected which may permit the full utilization of the sensitiveness of the present pressure-measuring apparatus.

The equation used to relate the pressure to the temperature is of the form employed for ammonia and carbon dioxide

$$\log p = -\frac{a}{T} + m + bT + cT^2 + dT^3 + \dots \quad (1)$$

The evaluation of the constants of this equation can sometimes, as was illustrated in the case of ammonia and carbon-dioxide, be best attained by using the equation in the "critical-constants" form⁷

$$\log p = -\frac{Z(T_c - T)^2 + \omega}{T} + m \quad (2)$$

In the case of methane, however, it was found to be preferable to select the approximate equation $\log p = -\frac{a'}{T} + m'$ and, by comparing the calculated with the observed logarithms of the pressures, obtain values designated as

$$\Delta \log p = \log p_{\text{obs}} - \log p_{\text{calc}}$$

These values were then plotted with the reciprocal of the cor-

⁷ Thermodynamic Properties of Ammonia. Keyes and Brownlee, Wiley & Sons, page 10, 1916

responding absolute temperatures and the best curve drawn to represent the final relation. The curve was then represented by means of the equation

$$\Delta \log p = -\frac{\Delta a}{T} + \Delta m + bT + cT^2 + dT^3$$

where Δa and Δm are constants which can be used in comparing with the approximate equation to give the final equation for $\log p$ as a function of the absolute temperature. The final equation is as follows where $T = (t + 273.13)$

$$\log_{10} p^{\text{atm}} = -\frac{595.546}{T} + 8.09938 - 4.04175 \times 10^{-2} T + 1.68655 \times 10^{-4} T^2 - 2.51715 \times 10^{-7} T^3 \quad (3)$$

TABLE III
Methane Vapor Pressure Data

<i>Temperature Deg. Abs.</i>	<i>Vapor Pressure Calc. Atms.</i>	<i>Temperature Deg. Abs.</i>	<i>Vapor Pressure Calc. Atms.</i>	<i>Temperature Deg. Abs.</i>	<i>Vapor Pressure Calc. Atms.</i>
95.00	0.1982	125.00	2.670	160.00	15.74
100.00	0.3444	130.00	3.641	165.00	19.14
105.00	0.5646	135.00	4.853	170.00	23.05
110.00	0.8813	140.00	6.338	175.00	27.49
111.52	1.0000	145.00	8.132	180.00	32.51
115.00	1.319	150.00	10.27	185.00	38.15
120.00	1.905	155.00	12.79	190.00	44.42
				191.03 Crit	45.79

In Table III will be found the vapor pressures in atmospheres for each five degrees beginning with 95° abs and ending with the critical pressure. The critical temperature and pressure were directly observed and may be compared with the value given by Cardoso* of -82.85° , as compared with -82.10° obtained in the present investigation.

Cardoso worked under great difficulties in connection with his thermometry and exercised the greatest care and skill in the construction of his pentane thermometers. Difficulties were encountered also in connection with the lag in the expansion and

* Cardoso, Jour. de Chim. Phys. **13**, 332, 1915.

contraction of the glass comprising the thermometers, so that in spite of all the precautions taken errors of temperature were difficult to avoid

In Table IV will be found the pressures given by Cardoso at the temperature observed with his pentane thermometer. The pressure measurements were made with a closed manometer, using the usual precautions to insure accuracy. It will be noted in the table that the Cardoso pressures are uniformly higher than those calculated by the Equation (3) and that the differences in temperature corresponding thereto are roughly the same order of magnitude, except the datum at 176.14° . The average temperature difference amounts to 0.56° and this correction applied to Cardoso's temperatures would bring the corresponding pressures into fair accord with the present measurements*. It will be noted in the

TABLE IV
Cardoso Vapor Pressure Data

T	188.74	187.54	185.14	182.14	178.14	176.14
$p_{\text{Cardoso}}^{\text{atms}}$	43.85	42.03	38.88	35.40	31.00	29.40
$p_{\text{cal}}^{\text{atms}}$	43.226	41.242	38.312	34.847	30.577	28.586
Δp	624	788	568	553	422	814
ΔT	49	63	48	49	42	84

Mean $\Delta T = 0.56$

Correcting T crit of Cardoso gives -82.29
 T crit M I T -82.11
 Olszewski 1885 -81.8
 p crit Cardoso $45.6 \text{ atms} \pm 0.1$
 p crit M I T 45.8 atms

* Cardoso, in verifying the readings of his pentane thermometer, used the freezing point of toluene, accepting a value for the freezing point, due to Timmermans, in 1912, of -94.5 . In this laboratory, there has been found for pure toluene -95.70 referred to the H_2 constant volume scale. Recently Timmermans, Van der Horst and Onnes (Chem. Ab. June 10, p. 1694, 1922) give -95.1 .

table that the critical pressure given by Cardoso is in good agreement with the pressure observed in this investigation. The temperature of the critical condition would, of course, be independent of any thermometer and a correction of 0.56 applied to the critical temperature, as observed with the pentane thermometer, would give -82.29 , which is not in bad agreement with -82.11 obtained in these measurements, since the temperature of the critical phenomenon is difficult to locate exactly and, moreover Cardoso has shown that it is best to stir the liquid in observing

Fig. 4

the critical temperature, whereas in this work no stirring was employed. In the section wherein the densities of liquid methane are presented it will be shown that a correction of about 0.6° in Cardoso's temperature brings his densities into good agreement with the new values.

In Fig. 4 the deviations of the individual pressure measurements of Tables 1 and 2 from the pressures calculated by means of Equation (3) are presented. The results obtained by Cardoso have been also inserted. It is evident that Equation (3) represents the new measurements as satisfactorily as can be expected.

5 The Specific Volumes of the Liquid and Vapor Phases.

The apparatus, Fig 2, used to measure the liquid specific volumes has already been described in connection with the vapor pressures. The method is of general applicability for the measurement of the liquid specific volumes for all substances whose critical temperature lies below the freezing point of mercury. The procedure, however, of confining the liquid in the volumenometer E by means of the gas phase requires that the mass of fluid in the gas phase, including that portion in the reservoir F, be determinable from a knowledge of its pressure, volume and temperature. This requirement has been met, in the present instance, from a knowledge of the methane equation of state, but empirical use of the experimental isotherms of gaseous methane could also be made.

The volume of the volumenometer between the engraved marks on the capillaries was 1.5798 cc, while the used volume of the reservoir was about 56 cc. The total quantity of methane employed amounted to about 0.66 g to 0.78 g, most of which would reside in the volumenometer at the lowest temperatures, but in the bell F at the highest. Owing to the relatively large fraction of the total mass of methane being contained in the reservoir and in the capillary leads of the volumenometer, the accuracy of the specific volume measurements becomes rapidly impaired near the critical temperature. Measurements, however, were carried out to 190.38 or within about 0.65 degree of the critical temperature. The latter temperature was observed directly, but the reliability of the observation would have been much enhanced by stirring the fluid, as has been pointed out in particular by Cardoso.

The actual density measurements for the two series of measurements are presented in Table V. For the greater part two observations at the same temperature setting were made at different times, which give a means of judging of the reproducibility of the method. It will be observed that the concordance is satisfactory on the whole, although in some instances (181.20°, Series A) a large difference (one part in 230) occurs. On the average, however, one part in fifteen hundred or better is attainable in individual measurements. The entire range of the liquid phase has been practically covered and the "smoothed values" are those obtained

TABLE V
Methane Liquid Densities

Series A			Series B		
Temperature Deg Abs	Density Liquid gm /c c. Obs.	Density Liquid gm /c.c. Smoothed	Temperature Deg. Abs.	Density Liquid gm./c.c. Obs.	Density Liquid gm /c c. Smoothed
186 143	.2505	.2504	128 562	.3980	.3989
186 143	.2504	.2504	128 562	.3979	.3989
181 203	.2768	.2762	123 911	.4051	.4059
181 203	.2756	.2762	123.911	.4049	.4059
178 189	.2882	.2881	119.249	.4129	.4128
178 189	.2879	.2881	119.249	.4127	.4128
172 437	.3067	.3067	114.631	.4196	.4196
172 437	.3067	.3067	114 631	.4195	.4196
168 351	.3186	.3182	110 023	.4266	.4263
168 351	.3185	.3182	110 023	.4262	.4263
163 295	.3312	.3312	106 003	.4313	.4321
163 295	.3313	.3312	105 451	.4329	.4329
158 339	.3429	.3429	100.903	.4394	.4394
158 339	.3426	.3429	153 193	.3542	.3544
153 385	.3531	.3540	158 171	.3439	.3433
153 385	.3531	.3540	181 100	.2768	.2766
148 439	.3631	.3644	186 054	.2510	.2509
143 495	.3752	.3741	187.974	.2366	.2375
143 495	.3750	.3741	188 937	.2279	
138 558	.3828	.3829	189 902	.2170	
138 558	.3832	.3829	190.381	.2093	
133 628	.3907	.3910			
133 628	.3909	.3910			
128 704	.3985	.3987			
128 704	.4000	.3987			

by plotting the densities rather than the specific volumes. Two densities at the extreme temperature ends of the liquid phase were chosen, and a linear equation determined from which deviations of each observed datum could be computed. By plotting these deviations with the corresponding temperatures a smooth curve could be drawn, from which the values tabulated as smoothed were read. The device is evidently equivalent to the construction of a very large plot of the observed data.

There have been found in the literature only the data of Cardoso already briefly referred to in the section dealing with the vapor pressure. It was pointed out in the latter section that the temperatures recorded by Cardoso appeared by comparison of the

TABLE VI
The Cardoso Saturation Specific Volumes

<i>T</i>	<i>V</i> ₁ <i>Cardoso</i>	<i>V</i> ₂ <i>Cardoso</i>	<i>V</i> ₁ <i>M I T</i> <i>from Mean</i> <i>Dens Equa</i>	<i>V</i> ₂ <i>M. I T</i>	<i>Cardoso</i> <i>V</i> ₁ <i>Corr</i>	<i>Cardoso</i> <i>V</i> ₂ <i>Corr.</i>
166 1	32 05	3 085	32 85	3.076	32 92	3 071
173 1	23 20	3 307	23 75	3 280	23 80	3 288
178 1	18 80	3 500	19 02	3 465	19 29	3 476
179 1	17 18	3 559	18 15	3 510	17 65	3 532
183 1	14 73	3 791	15 05	3 732	15 15	3 752
187 1	10 96	4 198	12 25	4 110	11 33	4 147
188 1	10 08	4 371				
189 1	9 15	4 628				

pressures to differ by 0.56° from the temperature scale used in this investigation. A shift in the Cardoso temperature scale of equal amount in this instance also brings the latter's observations into agreement with those here presented, thus confirming the opinion already stated that it is the temperature scales which are in disagreement rather than the pressure or volume measurements. In Table VI the second column gives the vapor volumes as given for the temperatures specified by Cardoso. The third column gives the Cardoso liquid volumes. Columns four and five contain the vapor and liquid volumes obtained in the present investigation at the same temperatures, and the sixth and seventh columns, the volumes of Cardoso corrected for the temperature difference 0.56. It is seen that substantial agreement is obtained, as was the case with the vapor pressures.

The specific volumes of the saturated vapor have always been exceedingly difficult to measure. The difficulty of obtaining true equilibrium, freedom from foreign gases, the complete drainage of the walls of the container, the relatively large fraction of the total mass necessarily present in the liquid phase, and surface adsorption are some of the difficulties encountered. Experimental experience has led almost to the conviction that the vapor specific volume cannot be accurately measured. In the case of ammonia it was found that the equation of state gave saturated vapor specific volumes which accorded with the actual observation within the unavoidable errors of experiment and the same statement is true as regards carbon dioxide.⁹ At the low temperatures

⁹ Keyes and Kenney, Jour. of Soc. Am. Ref. Engr., **3**, 1, 1917.

Fig. 5

encountered in the liquid range of methane some apprehension was felt concerning the reliability of using the methane equation of state to calculate the saturation specific volumes, but the enhanced difficulties of carrying out measurements at such low temperatures lead to the decision to calculate the volumes. In the case of nitrogen whose equation of state we possess, values are obtained which, when employed in the Clapeyron equation, give a value for the latent heat of vaporization agreeing well with the experimental number. It is, of course, evident that for the very large specific volumes (1,000 cc/g) the equation of state would be accurate. The doubt which may arise pertains to volumes from 200 cc/g to 30 cc/g.

The plot of a number of the isometrics of methane is represented in Fig 5, upon which has been placed the vapor pressures. The saturation specific volumes are the points of intersection of the isometrics with the pressure-temperature curve and this is, perhaps, the most convenient means of obtaining the vapor specific volumes. The final specific volumes for both phases are represented in the plot Fig 6.

Table VII contains the saturation specific volumes and densities of methane vapor and liquid from 95° to the critical temperature for each five degrees. Volumes smaller than 35 cc/g were not

Fig. 6

computed, since association or polymerization may be supposed to exist in the smaller volumes and the equation of state applies only for the case where the completely unassociated methane molecules are present. The mean diameter equation can be used to obtain volumes smaller than 35 cc/g

TABLE VII
M. I. T. Methane Data

<i>Temp Deg Abs</i>	<i>Specific Volume Liquid cc / gm</i>	<i>Specific Volume sat'd vapor Keyes' eq cc / gm</i>	<i>Density Liquid gm / cc</i>	<i>Density sat'd vapor Keyes' Eq gm / cc</i>	<i>Density sat'd vapor from dm and Liquid Density gm / cc</i>
95		2436.7		.0004104	
100	2.2691	1470.4	.4417	.0006801	
105	2.3069	936.9	.4335	.001067	
110	2.3458	624.7	.4263	.001601	
111.52	2.3580	556.9	.4241	.001796	
115	2.3865	432.7	.4190	.002311	
120	2.4291	309.4	.4117	.003232	
125	2.4735	227.4	.4043	.004398	
130	2.5208	171.0	.3967	.005850	
135	2.5719	131.0	.3888	.007632	
140	2.6288	102.1	.3804	.009794	
145	2.6937	80.63	.3712	.01240	
150	2.7683	64.43	.3612	.01552	
155	2.8533	51.96	.3505	.01925	
160	2.9491	42.22	.3391	.02369	
165	3.0496	34.49	.3279	.02899	
170	3.1881		.3137		.03667
175	3.3463		.2988		.04592
180	3.5565		.2812		.05598
185	3.8871		.2573		.07335
190					
191.03 Crit	6.2		.1613		.1613

The data of Cardoso relative to the saturation volumes were taken close to the critical temperature. However, in the range where the specific volumes were computed by means of the equation of state the following mean density equation was obtained

$$Dm = 0.16134 + 0.00065723 (T_c - T)$$

Cardoso gives the mean density equation based on his results,

$$Dm = 0.1623 + 0.0006064 (T_c - T)$$

The agreement is very good and lends confidence to the computed

values Fig 7 gives the densities obtained in the present investigation together with the uncorrected Cardoso values. The critical density, making the temperature correction 0.56, makes the critical density of Cardoso 0.1618, as compared with 0.1613 obtained in the present investigation.

Fig. 7

6 The Latent Heats of Evaporation. A preliminary study has been made in the development of calorimetric methods that will permit the measurement of heats of evaporation and the specific heats of liquids at very low temperatures. At present, however, no experimental values are available for methane, but by means of the vapor pressure equation and the specific volumes of the coexisting phases, latent heats may be calculated by means of the Clapeyron equation.

The equation of the vapor pressure, (3), upon differentiation gives for $\frac{dp}{dt}$,

$$\frac{dp}{dT} = p \left[\frac{1371.298}{T^2} - 0.093065 + 7.76685 \times 10^{-4} T - 1.73878 \times 10^{-6} T^2 \right] \quad (4)$$

In Table VIII will be found in the first column the absolute temperature and in the succeeding columns the value of $\frac{dp}{dT}$,

TABLE VIII
Latent Heat of Evaporation

T	$\frac{dp}{dT} \text{ atms}$	$V_1 \frac{cc}{g}$	$V_2 \frac{cc}{g}$	$\lambda \frac{cal}{g}$	$calc$
100	0 03593	1470 4	2 2691	127 75	127 59
105	0 05290	936 9	2 3068	125 71	125 71
110	0 07461	624 7	2 3458	123 69	123 76
111 52	0 08214	556 8	2 3580	122 99	Normal Boiling Pt
115	0 10152	432 7	2 3868	121 65	121 74
120	0 13403	309 4	2 4291	119 58	119 64
125	0 17249	227 4	2 4735	117 44	117 44
130	0 21723	171 0	2 5208	115 19	115 14
135	0 26856	131 0	2 5719	112 79	112 71
140	0 32677	102 7	2 6288	110 20	110 14
145	0 39214	80 6	2 6937	107 32	107 39
150	0 46493	64 4	2 7683	104 14	104 44
155	0 54535	51 96	2 8533	100 52	101 23
160	0 63363	42 22	2 9491	96 42	97 70
165	0 72975	34 49	3 0496	91 68	93 74

V_1 , V_2 and the latent heat On the basis of these latent heat values the following equation was composed relating the quantity to the temperature

$$\log_{10} \lambda = 1.65214 + 2.0076 \times 10^{-4} (T_c - T) + 0.22225 \log_{10} (T_c - T). \quad (5)$$

There are no published data for the latent heat of evaporation of methane with the exception of an approximate value recently obtained due to Satterly and Patterson¹⁰ who give 138 cal/g $\pm 5\%$. This value refers to the temperature of the normal boiling point 111.52° at which temperature 123 cal/g is obtained in the present investigation. The experimental value is about ten per cent greater. The value of the mean specific heat of copper is involved in the measurement and an error in the true boiling point of methane enters in computing the latent heat from the experimental data. The methane evolved by the copper block dropped into the liquid was measured by collecting over water. In a later paper experimental values obtained in this laboratory will be presented.

If the liquid phase consisted of completely polymerized double molecules or, in fact, was composed of molecules whose molecular

¹⁰ Satterly and Patterson, Roy Soc Can Trans **13**, 123, 1919

species was constant with respect to temperature changes the internal heat of evaporation would be simply related to the specific volumes of the coexisting phases. Consider the thermodynamic equation:

$$\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial p}{\partial T}\right)_v - p \quad (6)$$

Integration of this equation at constant temperature yields,

$$U_2 - U_1 = \int_{v_1}^{v_2} \left(T \left(\frac{\partial p}{\partial T}\right)_v - p \right) dv \quad (7)$$

and for an invariable species composing the liquid phase of specific volume, v_2 , passing to a specific volume v_1 of the vapor phase the energy is represented by the work against the attractive forces of the molecules. Evaluating $\left(\frac{\partial p}{\partial T}\right)_v$ by means of the equation of state will give, then, a definite value for the right-hand member of Equation (7)

$$\int_{v_1}^{v_2} \left(T \frac{\partial p}{\partial T} - p \right) dv = \int_{v_1}^{v_2} \left(\frac{RT}{v-\delta} - p \right) dv = \int_{v_1}^{v_2} \frac{A}{(v-l)^2} dv,$$

or

$$\Delta U = U_1 - U_2 = A \left(\frac{1}{v_2-l} - \frac{1}{v_1-l} \right). \quad (8)$$

Now ΔU and the specific volumes of the coexisting phases may be plotted with $\frac{1}{\Delta U}$ and v_2 as coordinates giving a line which may be used as an approximation plot to roughly evaluate l and A and the data replotted, using as coordinates $\frac{1}{\Delta U + \frac{A}{v_1}}$

and v_2 . The fact that a straight line is obtained may mean that the molecular state of the liquid is the same as that of the vapor in contact therewith, or it may mean that the molecular state of the liquid, for example, was that of substantially complete polymerization to double molecules or those of higher order, the vapor in

contact consisting of substantially all single molecules. The value of A in the latter case would be a certain mean value, then, between the value of A for double molecules and single molecules. If the liquid, however, was composed of molecules of the same type as the vapor, the value of A should be numerically equal to

Fig. 8

A obtained for the equation of state of methane. Moreover, if the data do not lie on a straight line in terms of the coordinates given, evidence is afforded that the relative molecular state in the coexisting phases is changing at higher temperatures. As a matter of fact the data of methane in the lower temperature range do lie on a straight line, but deviate at higher temperatures.

are approached. Also the numerical value of A is not that found for the equation of state of methane composed of single molecules. Fig. 8 exhibits the methane data.

The further elaboration of the connection between the internal heat of evaporation and the equation of state has been waiting for some years for the completion of several investigations in progress in this laboratory. Very shortly, for example, there will appear the results in connection with liquid ether at low temperatures, which illustrate the linear relation between $\frac{1}{\Delta U + \frac{A}{v_1}}$ and v_2 , and further papers, it is hoped, will follow promptly.

7 The Specific Heats of the Coexisting Phases. The experimental data for the vapor phase have been published by Regnault,¹¹ Lussana¹² and Heuse.¹³ The latter data supersede the older work and measurements were made at the temperatures 15.0, 5.0, -30.0, -55.0, -81.0. The one atmosphere constant pressure values were computed to constant volume specific heats by means of the equation of state and from a plot values chosen at the absolute temperatures 150, 200, 250, 300 for the purpose of correlation as a function of the temperature. The equation obtained is,

$$C_p = 0.3050 + 1.12 \times 10^{-3} T - 6.45 \times 10^{-6} T^2 + 13.04 \times 10^{-9} T^3. \quad (9)$$

To obtain the constant pressure specific heat use may be made of the equation

$$C_p = C_v + T \left(\frac{\partial p}{\partial T} \right)_v \left(\frac{\partial v}{\partial T} \right)_p \quad (10)$$

which becomes using the equation of state for methane

$$C_p = C_v + \frac{R/m}{1 - \frac{a\delta}{v^2} - \frac{2A}{RT} \frac{(v-\delta)^2}{(v+l)^3}} \quad (11)$$

This equation is not valid in the critical region but will give accurate values along the saturation line to at least 35 c.c. per

¹¹ Regnault. *Mem. de l'Acad.* **26**, 1, 1862.

¹² Lussana. *Nouv. Cim.* **36**, 5, 70, 130, 1894.

¹³ Heuse. *Ann. d. Phys.* **59**, 94, 1919.

gram For low pressures it suffices to replace (11) by the approximate equation

$$C_p = C_{p_0} + \frac{2A}{R} \cdot \frac{1}{T^2} p \quad (12)$$

where C_{p_0} is the specific heat at very low pressures, being equal to $C_v + R/m$; m representing the molecular weight in grams and R the gas constant per mol in calories The numerical equation corresponding to (12) is,

$$C_p = 0.4288 + 1.12 \times 10^{-3} T - 6.45 \times 10^{-6} T^2 + 13.04 \times 10^{-9} T^3 + \frac{93}{T^2} p^{\text{atm}} \quad (13)$$

In Table IX will be found the comparison of the vapor specific heats computed by Equation (9) and the experimental values due to Heuse

TABLE IX
The Gas Phase Specific Heat

	15 0	5.0	-30 0	-55 0	-81 0
C_v Heuse	0.4051	0.4000	0.3826	0.3782	0.3777
C_v Calculated	0.4041	0.3982	0.3834	0.3778	0.3746

Regnault gives 0.593 cal as the value of C_p between 18 and 208 at one atmosphere Equation (13), however, leads to 0.675 cal Lussana gives 0.591 cal between 11 and 95 at one atmosphere, whereas the equation gives 0.564 cal Lussana gives the specific heat between 11 and 95 as a function of the pressure, as follows:

$$C_p = 0.5915 + 0.03463(p-1)$$

whereas Equation (13) leads to

$$C_p = 0.5643 + 0.00089(p-1).$$

The pressure coefficient of Lussana is nearly forty times as large as that given through the equation of state In the case of air Lussana's pressure coefficient is also much greater than that given by the equation of state for air¹⁴ Holborn and Jacobs,¹⁵

¹⁴ Keyes, Jour. Amer. Chem. Soc. **43**, 1452, 1921.

¹⁵ Holborn and Jacobs, Z. Ver. deut. Ing. **58**, 1429, 1914.

however, recently measured the specific heat of air to 200 atms. and their mean pressure coefficient agrees almost exactly with that given through the equation of state. Carbon dioxide and ammonia furnished further examples and there can be little doubt but that Lussana's pressure coefficients are all too large.

Facilities for measuring the specific heat of the liquid phase of substances have been under development for some years and shortly values will be available. In the meantime use may be made of the available data to calculate the liquid phase specific heat.

Consider the thermodynamic equation

$$C_{s_1} - C_{s_2} = T \frac{d\lambda}{dT} \quad (14)$$

where C_{s_1} and C_{s_2} denote the specific heat of the saturated gas and liquid phases respectively, while λ as before represents the latent heat of evaporation. The equation for C_{s_1} is,

$$C_{s_1} = C_{p_1} - T \left(\frac{\partial v}{\partial T} \right)_p \frac{dp}{dT}$$

and $C_{p_1} = C_v + T \left(\frac{\partial p}{\partial T} \right) \cdot \left(\frac{\partial v}{\partial T} \right)$. By means of the equation of state the differential coefficients can be evaluated, while C_v is given by the equation (9). The equation for $T \frac{d\lambda}{dT}$ can be formed from Equation (5) leading to

$$T \frac{d\lambda}{dT} = -\lambda \left[0.0004623 + \frac{0.22225}{T_c - T} + \frac{1}{T} \right].$$

At 110° C_{s_1} is $-0.689 \frac{\text{cal}}{\text{g}}$ and $T \frac{d\lambda}{dT}$ equal to -1.522 , giving C_{s_2} ,

the specific heat of the liquid, $0.833 \frac{\text{cal}}{\text{g}}$. At 150° C_{s_1} is $-0.489 \frac{\text{cal}}{\text{g}}$

and $T \frac{d\lambda}{dT}$ equal to -1.307 giving $0.818 \frac{\text{cal}}{\text{g}}$ for the liquid specific

heat. The latter number would be expected to be larger than the former, but the specific heat value at 110° involves a long extrapolation by means of the gas phase constant volume specific heat Equation, (9) All that may be stated at present is that in the region of the boiling point the specific heat of the liquid is about $0.82 \frac{\text{cal.}}{\text{g.}}$

SUMMARY

1 The vapor pressure of methane has been measured over substantially the entire liquid phase region and correlated as a function of the temperature as follows.

$$\log_{10} p^{\text{atm.}} = -\frac{595\,546}{T} + 8\,09938 - 4\,04175 \times 10^{-2} T + 1\,68655 \times 10^{-4} T^2 - 2\,51715 \times 10^{-7} T^3.$$

2 The liquid phase specific volumes have been measured from about 100° abs to nearly the critical temperature, 191.03 abs. The saturation specific volumes of the vapor phase were computed by means of the equation of state of methane, using the values of the pressure computed for definite temperatures from the vapor pressure equation.

3 The critical temperature is found to be 191.03° abs on the scale of the quartz constant volume hydrogen thermometer. The critical pressure amounts to 45.8 atms, while the critical volume computed from the mean diameter equation is 6.2 cc/g.

4 The heat of evaporation was computed by the Clapeyron equation, using the derivative $\frac{dp}{dT}$ obtained by differentiation of the vapor pressure equation and the specific volumes of the coexisting phases. The following equation reproduces the values from 100° abs to 150° abs where λ represents the heat of evaporation:

$$\log_{10} \lambda = 1\,65214 + 2\,0076 \times 10^{-4} (T_c - T) + 0\,22225 \log_{10} (T_c - T).$$

5 The specific heat of the gas phases may be represented by the following equation based on the experimental values of Heuse:

$$C_v = 0.3050 + 1.12 \times 10^{-3}T - 6.45 \times 10^{-6}T^2 + 13.04 \times 10^{-9}T^3.$$

6 The specific heat of the saturated liquid was computed by means of the thermodynamic equation

$$C_{s_2} = C_{s_1} - T \frac{d\lambda}{dT}$$

and found to be $0.82 \frac{\text{cal.}}{\text{g.}}$ in the neighborhood of the normal boiling point