Numerical Calculations

Corresponding to the absolute correction $-\Delta\gamma$, we define $-\Delta\mathrm{E}^s$ and $-\Delta\bar{\gamma}$ as the corrections to E_0^s and γ_0, owing to curvature, as given by Eqs. (13) and (25). Table **I** gives $\Delta\gamma$, $\Delta\mathrm{E}^s$ and $\Delta\bar{\gamma}$ as a function of r_0 for argon at 90°K., using[2] $a = 1.11 \times 10^{-10}$ erg-Å.[6] and density = 1.374 g./cc. For the smaller values of r_0, the number of argon atoms in a sphere of radius r_0 (with the bulk liquid density) is also given as a matter of interest. Incidentally, we find $\mathrm{E}_0^s = 27.2$ dyne/cm., in agreement with Kirkwood and Buff, but obtain $\gamma_0 = 14.5$ dyne/cm. instead of[2] 14.9 dyne/cm.

TABLE I

EFFECT OF RADIUS ON SURFACE TENSION AND SURFACE ENERGY OF ARGON AT 90°K.

($\gamma_0 = 14.5$ dyne/cm. and $\mathrm{E}_0^s = 27.2$ dyne/cm.)

r_0, Å.	$\Delta\gamma$, dyne/cm.	$\Delta\bar{\gamma}$, dyne/cm.	$\Delta\mathrm{E}^s$, dyne/cm.	No. atoms in drop
15	0.14	0.76	0.81	293
20	.08	.47	.51	694
25	.05	.32	.34	1356
50	.012	.09	.11	..
100	.003	.02	.02	..

Bearing in mind the approximate nature of the model (especially for small r_0), the conclusion reached on the basis of Eq. (34) and Table I is that, although the surface tension and surface energy decrease with decreasing radius, the magnitude of the effect appears to be surprisingly small. It is of course quite possible that calculations based on a more rigorous model will alter these conclusions; this remains to be seen. In particular, aside from compressibility, the refinements of taking into account the alteration of $g(r)$ and ρ_0 near a surface—*especially* a curved surface, of course—may prove to be important. In the meantime, the present paper provides the extension of Fowler's approximate model to curved surfaces, and should be considered only a zero-order approximation.

Acknowledgment.—The author is indebted to Professor E. O. Wiig for his encouragement, to the Chemical Corps Technical Command for its financial support of most of this investigation, and to Professor J. G. Kirkwood and Dr. F. P. Buff for their helpful comments.[9]

Summary

The approximate model used by Fowler to investigate theoretically the surface energy and surface tension of a plane liquid surface is extended to spherical drops and bubbles, with the additional assumption of liquid incompressibility. It turns out to be possible to derive a very simple expression for the correction (to the plane surface tension) owing to curvature, which predicts that the surface tension decreases with radius. However, the magnitude of the effect is not large in this zero-order approximation.

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(9) NOTE ADDED IN PROOF: For some very recent publications on this subject, see V. K. LaMer and G. M. Pound, *J. Chem. Phys.*, **17**, 1337 (1949); *ibid.*, in press; F. P. Buff and J. G. Kirkwood, *ibid.*, **18**, 991 (1950); F. O. Koenig, *ibid.*, **18**, 449 (1950); J. L. Shereshevsky and Carter, THIS JOURNAL, **72**, 3682 (1950).

BETHESDA, MD. RECEIVED DECEMBER 14, 1949

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

The Vapor Pressure of Normal Hydrogen from the Boiling Point to the Critical Point[1]

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

Introduction

The accurate determination of the vapor pressure of liquid hydrogen leads to simple, yet accurate, means of evaluating many thermochemical properties, which are difficult to obtain by direct experiment. Earlier determinations of the vapor pressure of hydrogen at the Physical Reichsanstalt in Berlin[2] and at the Leiden University Cryogenic Laboratory[3] and the recent work at the National Bureau of Standards,[4] are sufficiently accurate in the neighborhood of the boiling point. However, the only data at higher pressures were obtained at Leiden in 1917, before means of good temperature control in the region 20–35°K. had been developed. The type of cryostat employed by the Leiden workers was a vapor bath.[5] With this type of cryostat it is difficult to attain and to maintain temperature equilibrium.

A vapor-bath cryostat of the same type was tried in this Laboratory and found to be unreliable. We found it extremely difficult to maintain the glass vessel, containing the liquid, at the same temperature as the gas stream, and thermal equilibrium was often not attained even after three or four hours.

The Preparation of the Hydrogen.—The hydrogen was prepared electrolytically, and purified by three successive liquefactions and distillations. Subsequent to this purification, the gas was stored for several months at 150 atmospheres pressure in a previously evacuated steel

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(1) This work was supported in part by the Air Materiel Command under contract with The Ohio State Research Foundation.

(2) Henning, *Z. Physik*, **40**, 775 (1926).

(3) (a) P. G. Cath and H. K. Onnes, *Leiden Comm.*, No. 152a (1917); (b) J. Palacios Martinez and H. K. Onnes, *ibid.*, No. 156b (1922); (c) Keesom, Bijl and Horst, *ibid.*, No. 217a (1931); (d) Onnes and Keesom, *ibid.*, No. 137d (1913).

(4) H. W. Wooley, R. S. Scott and F. G. Brickwedde, *J. Research Natl. Bur. Standards*, **41**, 379 (1948), RP 1932.

(5) H. K. Onnes, *Leiden Comm.*, No. 151a (1917).

cylinder. Just before use, the gas was analyzed for traces of nitrogen and other inert constituents by the methods of Dodge[6] and of Kanolt and Cook.[7] The method of Winkler[8] was used to analyze for traces of oxygen. The total impurity in the hydrogen was found to be *less* than 0.002 mole per cent.

Apparatus.—The apparatus used for these experiments will be described in a separate paper from this Laboratory.[9] The temperature of the vessel containing liquid hydrogen was measured by the same two copper–constantan thermocouples used in that apparatus. Temperatures were read with a precision of 0.002° and with an accuracy of 0.02°K.

Lower pressures were measured with an absolute mercury manometer, and pressures from about 1.5–2.5 atmospheres were measured with an open-end mercury manometer. The manometers were read with a cathetometer which was accurately calibrated to 0.03 mm. For pressures greater than 2.5 atmospheres, a modified M.I.T.-type dead-weight gage[10] was used. The calibration and use of this gage has been previously outlined.[9] At lower pressures the dead-weight gage has a precision of one part in ten thousand, whereas at higher pressures the gage is precise to one part in thirty thousand.

Experimental Techniques and Results.—Three series of runs, A, B and C, were made, using separate fillings from the same cylinder of pure hydrogen for each series. The first series was limited to three points and was intended to prove the adequacy of the experimental techniques. The second, conducted two months later, consisted of twelve points taken in consecutive order from a little above the boiling point to 31.40°K. The twelve points were taken within a period of six hours. The third series, made with a fresh filling of hydrogen on the day following series B, consisted of two points both taken within an hour.

The following description of the techniques employed is applicable to the final two series. After cooling the pipet to the boiling point of hydrogen, pure hydrogen gas was introduced until the pipet was partially filled with liquid. While a high vacuum surrounded the pipet, the blocks were brought to a temperature of about one-half degree above that of the pipet in order to make sure that there could be no condensation of vapor above the level of liquid in the pipet. As a preliminary to each run except the first, the temperature of the pipet and that of the blocks, was raised about one degree and approximately ten minutes allowed for thermal equilibrium. Then, to be sure that both liquid and vapor phases co-existed in equilibrium within the pipet, the procedure outlined below was followed.

(a) After reading the pressure, a small quantity of gas was added to the system to cause an instantaneous rise of about 0.1 atmosphere. Rapid return to within 0.01 atmosphere of the original pressure was taken to indicate the existence of a liquid phase.

(b) An equally small amount of gas was then removed from the system to bring about an instantaneous pressure drop of about 0.1 atmosphere. Rapid return to within 0.01 atmosphere of the original pressure was taken to indicate the existence of a vapor phase in equilibrium with a liquid[11] within the pipet.

(c) After repeating this procedure one or more times, the system was allowed to stand for a few minutes in order to regain thermal equilibrium. During this period, the potentiometer batteries were balanced, the temperature of the blocks determined, and the barometer read.

Readings of pipet temperature and pressure were then recorded at one-minute intervals for a period of nine minutes. The data were plotted and smoothed values read from the curves for the fifth minute. These smoothed values were adopted for the run. Table I presents the data for a typical run.

TABLE I

DATA OBTAINED IN A TYPICAL RUN, No. C2

Barometric pressure 751.1 mm. at 22.0°; piston factor for dead-weight gage, 0.0026351 atm./g.; sensitivity of thermocouple at 33° K. 8.5 μv./deg.

Time, P.M.	Thermocouple readings in microvolts Upper block	Lower block	Auxiliary block	Lower pipet	Upper pipet	Dead-weight gage load (piston 2)
5:02	6024	6024	6024			
5:05				6029.18		4319.0
5:06				6029.16		4319.0
5:07				6029.16		4319.2
5:08					6029.37	4319.4
5:09					6029.37	4319.5
5:10					6029.35	4319.7
5:11				6029.16		4319.9
5:12				6029.21		4320.1
5:13				6029.16		4320.3
5:15	6024	6024	6026			

The results obtained in the three series of runs are tabulated in the first three columns of Table II. Two points in the immediate neighborhood of the critical point have been included. These points were taken with a different apparatus and are described in our separate paper on the critical constants of hydrogen.[12]

TABLE II

VAPOR PRESSURE OF HYDROGEN

Run	No.	Temp., °K.	P(atm.) Obsd.	P(atm.) Calcd.	P(obsd. − calcd.)	T (obsd. − calcd.)
A	1	27.31	4.8956	4.9010	−0.0054	+0.01
A	2	28.85	6.4144	6.4276	− .0132	+ .01
A	3	32.00	10.6090	10.6280	− .0190	+ .01
B	1	20.90	1.1596	1.1568	+ .0028	− .01
B	2	21.81	1.4844	1.4830	+ .0014	.00
B	3	22.65	1.8155	1.8358	− .0203	+ .05
B	4	23.72	2.3493	2.3640	− .0147	+ .03
B	5	24.73	2.9510	2.9510	.0000	.00
B	6	25.70	3.6126	3.6035	+ .0091	− .01
B	7	26.74	4.4178	4.4091	+ .0087	− .01
B	8	28.20	5.7618	5.7464	+ .0154	− .02
B	9	29.56	7.2763	7.2381	+ .0382	− .03
B	10	30.19	8.0645	8.0194	+ .0451	− .03
B	11	30.79	8.8359	8.8216	+ .0143	− .01
B	12	31.40	9.6981	9.6993	− .0012	.00
C	1	32.36	11.2065	11.2181	− .0116	+ .01
C	2	33.07	12.3553	12.4592	− .104	+ .04
	[a]	33.244	12.797	12.782	+ .015	.00
	[a]	33.140	12.620	12.597	+ .023	− .01

[a] *Cf.* ref. 12.

Figure 1 presents a comparison of the vapor pressure data obtained at this Laboratory with those obtained at Leiden.[3a] A plot of the reciprocal of the absolute temperature versus the log of the pressure is given in Fig. 2. The curve of Fig.

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(6) Dodge, THIS JOURNAL, **45**, 1688 (1923).

(7) Kanolt and Cook, *Ind. Eng. Chem.*, **17**, 183 (1925).

(8) Winkler, *Ber.*, **21**, 2843 (1888).

(9) H. L. Johnston and I. Bezman, unpublished.

(10) F. G. Keyes, *Ind. Eng. Chem.*, **23**, 1375 (1931).

(11) The capillary dimensions were such that the small additions and withdrawals would correspond to liquid volumes in excess of the entire capillary volume; *cf.* ref. 9.

(12) D. White, A. S. Friedman and H. L. Johnston, THIS JOURNAL, **72**, 3565 (1950).

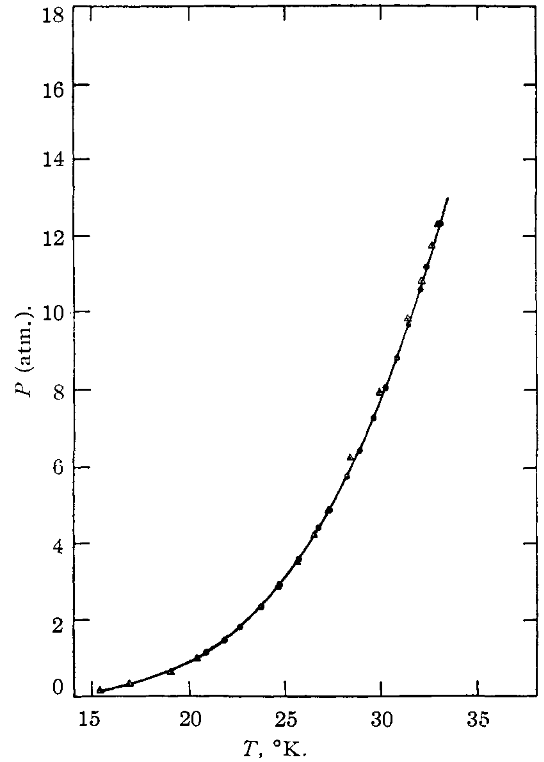

Fig. 1.—The vapor pressure of normal hydrogen: ⊙, the data of this research; △, the vapor pressure data of Cath and Onnes at Leiden (*Leiden Comm.*, No. 152a).

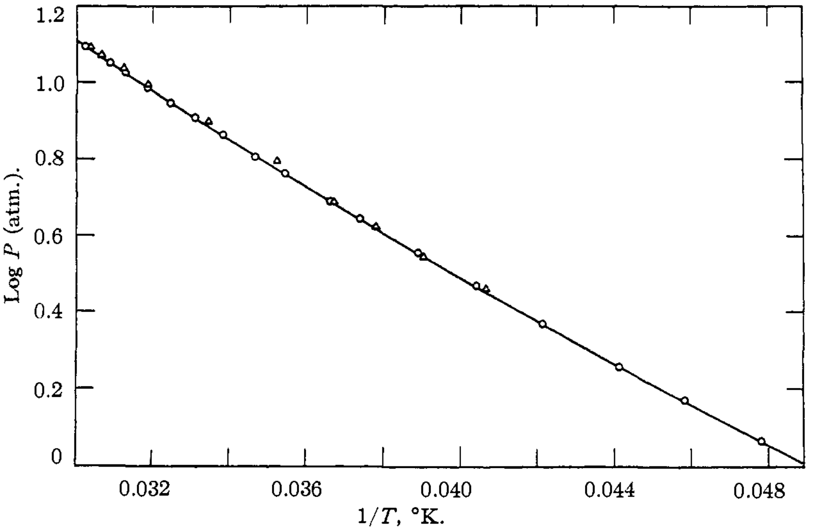

Fig. 2.—The vapor pressure of normal hydrogen. The logarithm of the vapor pressure plotted against the reciprocal of the temperature: ⊙, the data of this research; △, the data of Cath and Onnes at Leiden (*Leiden Comm.*, No. 152a).

2, including the two values obtained with the critical point apparatus, is expressed accurately by the equation

$$\log p_{\text{atm}} = a + b/T + cT + dT^2 \quad (1)$$

where the constants, obtained by the method of least squares, are

$a = 3.068281$; $c = -3.1282 \times 10^{-2}$
$b = -55.25642$; $d = 6.6989 \times 10^{-4}$

The equation yields 20.40°K. for the normal boiling point of hydrogen, which agrees with the accepted value of 20.38°K. within the limits of accuracy.

The apparatus used in this research was not adaptable to vapor pressure determinations in the region of the triple point. An attempt was made to obtain an equation which would include the vapor pressure data of other workers in this region, but no simple convenient equation was found which would represent all vapor pressure data and still be within the experimental accuracy of our determinations. However, our vapor pressure curve for the region above the boiling point smoothly joins the Natl. Bur. Standards vapor pressure curve[4] for the region below the boiling point. Vapor pressures calculated from our equation are still within the limits of experimental error for a few degrees below the boiling point, but begin to deviate slightly from the values obtained from the Natl. Bur. Standards equation as the triple point is approached. In the worst case, the deviation is about 0.009 atmosphere, which corresponds to a temperature deviation in excess of experimental error.

Latent Heat of Vaporization.—The latent heat of vaporization is related to the vapor pressure by the Clapeyron equation.

$$\frac{dP}{dT} = \frac{L_v}{T(V_g - V_l)} \quad (2)$$

By substituting equation (1) into the Clapeyron equation and rearranging terms

$$L_v = 0.05578\, T(V_g - V_l)P\left(-\frac{b}{T^2} + c + 2dT\right) \quad (3)$$

where L_v is expressed in units of the international thermochemical calorie per gram, and V_g and V_l represent specific volumes of the gas and liquid, respectively.

The data obtained by Mathias, Crommelin and Onnes[13] on the rectilinear diameter of hydrogen was used to get the specific volume of the liquid as a function of temperature. The specific volumes of the gas were obtained from the vapor densities of Mathias, Crommelin and Onnes,[13] which agree with vapor density data obtained in this Laboratory. Equation (3) was solved for various temperatures and pressures. The smoothed results obtained are shown in Table III and Fig. 3. Molal heats of vaporization, as well as latent heats are included in the table for convenience.

[13] Mathias, Crommelin and Onnes, *Leiden Comm.*, 154b (1918).

TABLE III

HEATS OF VAPORIZATION OF HYDROGEN

Temp., °K.	L_v cal./g.	ΔH cal./mole
20.40	108.5	218.7
22.0	105.5	212.7
24.0	100.7	203.0
26.0	94.6	190.7
28.0	86.1	173.6
29.0	80.5	162.3
30.0	73.6	148.4
31.0	64.4	129.8
32.0	50.7	102.2
32.5	40.0	80.6
32.75	32.5	65.5
33.0	20.0	40.3
33.1	15.0	30.2

Solution of equation (3), for a temperature of 20.40°K., yields 218.7 cal./mole for the molal heat of vaporization. This compares favorably with the computed value of 219.3 for normal hydrogen based on the accurate calorimetric value of 214.8 ± 0.4 for pure para hydrogen recently determined in this Laboratory.[14]

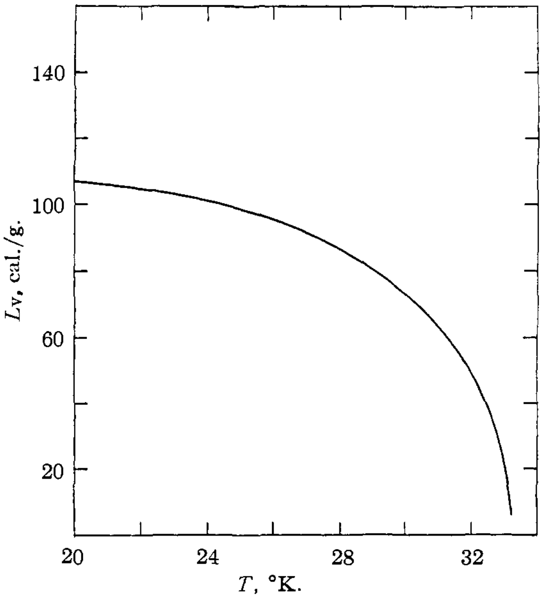

Fig. 3.—The latent heat of vaporization of hydrogen *versus* the absolute temperature.

***ortho-para* Content During the Experiments.**—The equilibrium concentration of para hydrogen at 25° is 25.0 mole per cent., whereas the equilibrium concentration of para hydrogen at 20°K. is 99.7 mole per cent. Freshly liquefied hydrogen should, therefore, have the normal 25% para content, but will change with time in the direction of 99.7% para content. The rate of conversion in very pure liquid hydrogen follows the second order rate law

$$dy/dt = -ky^2 \qquad (4)$$

where y is the mole fraction of ortho hydrogen at time t, and k is a constant equal to 2.00×10^{-4} per minute. In the presence of catalytic surfaces, and particularly in contact with particles of solid air this rate may be greatly increased. In earlier investigations of the vapor pressure of hydrogen[2,3] it was generally impossible to estimate how much conversion may have occurred from the normal mixture when vapor pressure data were taken. In our investigations, it is possible to show that the para content cannot have reached more than about 28.5% in the most unfavorable case. This value is only 3.5% higher than normal and can have little influence on the observed pressures.

The rate of conversion in our copper pipet should correspond to that given by equation (4) with k set equal to 2.00×10^{-4} since experiments carried out in a copper reaction vessel, in this Laboratory, established that constant for hydrogen of the same purity as that employed in the vapor pressure measurements. Integration of equation (4) for a time interval of 360 minutes indicates a drop in ortho hydrogen content from an initial 75 to a final 71%. Allowance for small additions of fresh hydrogen during the 12 runs of series B brings this final percentage to about 71.5% ortho. This is the deviation from normal composition that must have occurred for Run B 12 and is the maximum deviation that can have occurred in any of the 18 runs. This maximum deviation from the normal mixture corresponds to a vapor pressure increase of less than 0.2 of 1%, and is only slightly beyond experimental error.

Summary

The vapor pressure of hydrogen from the boiling point to the critical point has been determined and can be represented by the equation $\log p_{\text{atm}} = 3.068281 - 55.25642/T - 3.1282 \times 10^{-2}\,T + 6.6989 \times 10^{-4}T^2$. The boiling point calculated from this equation is 20.40°K.

The heat of vaporization at the boiling point as calculated from this equation is 218.7 cal./mole. This value is in good agreement with the value 219.3 cal./mole for normal hydrogen, computed by Johnston, Rifkin and Kerr from their accurate calorimetric value of 214.8 for pure para hydrogen.

COLUMBUS, OHIO RECEIVED FEBRUARY 3, 1950

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[14] H. L. Johnston, E. B. Rifkin and E. C. Kerr, THIS JOURNAL, **72**, in press (1950).