[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

The Compressibility of and an Equation of State for Gaseous Normal Pentane

BY JAMES A. BEATTIE, SAMUEL W. LEVINE AND DONALD R. DOUSLIN

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The compressibilities of normal pentane have been measured from 200 to 300° and from a density of 1 to 7 moles per liter, the maximum pressure being 350 atm. The constants of the Beattie–Bridgeman equation of state for normal pentane are $R = 0.08206$, $A_0 = 28.2600$, $a = 0.15099$, $B_0 = 0.39400$, $b = 0.13960$, $c = 400 \times 10^4$, molecular weight $= 72.0924$ in units of normal atm., liter per mole, °K. (T °K. $= t$, °C. $+ 273.13$). The second virial coefficients were also determined to three significant places from 200 to 300°.

The compressibility of normal pentane has been measured from 40 to 280° and to a maximum pressure of about 75 atm. by Rose-Innes and Young,[1] and from 38 to 238° and to a maximum pressure of 680 atm. by Sage and Lacey.[2] Our study extends from 200 to 300° and from a density of 1 to 7 moles per liter or a maximum pressure of 350 atm.

The experimental method has been described earlier.[3] In the present work the bomb with the glass liner was used. The same equipment has been employed in the study of the volumetric behavior of a number of hydrocarbons.[4]

TABLE I

CONSTANTS OF THE BEATTIE–BRIDGEMAN EQUATION OF STATE FOR NORMAL PENTANE

$$p = [RT(1 - \epsilon)/V^2][V + B] - A/V^2$$
$$A = A_0(1 - a/V)$$
$$B = B_0(1 - b/V)$$
$$\epsilon = c/VT^3$$

Units: normal atmosphere, liter per mole, °K. (T °K. $= t$ °C. $+ 273.13$)

$R = 0.08206$ $a = 0.15099$ $b = 0.13960$
$A_0 = 28.2600$ $B_0 = 0.39400$ $c = 400 \times 10^4$
Mol. wt. = 72.0924

We are greatly indebted to Dr. F. D. Rossini for supplying the purified sample of normal pentane which was made available through the American Petroleum Institute Research Project 44 and was purified at the National Bureau of Standards by the A.P.I. Research Program 6, under the supervision of Dr. Rossini. The stated purity was 99.85 ± 0.07 mole per cent. normal pentane.

The sample used in the present investigation weighed 7.1459 g. and was the same loading employed in a study[5] of the vapor pressure and the critical region. The behavior of the substance in these latter measurements indicated that it was of satisfactory purity.

The compressibilities of normal pentane determined in the present investigation are listed in Table II together with the deviations of the pressures calculated from the equation of state given in Table I from the observed pressures. In computing the compressor settings for even densities we used the value 72.0924 for the molecular weight of pentane (H = 1.0077, C = 12.000), and in fitting the equation of state to the measurements we used the value 273.13° for the Kelvin temperature of the ice point. These values were employed so that the present measurements and the constants of the equation of state of pentane are on a comparable basis with the earlier work of this laboratory on hydrocarbons.

TABLE II

COMPARISON OF THE PRESSURES CALCULATED FROM THE EQUATION OF STATE WITH THE OBSERVED PRESSURES FOR GASEOUS NORMAL PENTANE (C_5H_{12})

For each temperature the first line gives the observed pressure and the second line gives the observed minus the calculated pressure. The calculated pressures were computed from the equation given in Table I. The critical constants of n-pentane are: $t_c = 196.62°$ (Int.), $p_c = 33.31$ normal atm., $d_c = 3.39$ moles per liter, $v_c = 0.295$ liter per mole.

Density, moles/liter Temp., °C. (int.)		1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5	5.0	6.0	7.0
		Pressure, normal atmosphere										
200	obsd.	25.70	31.13	33.66	34.63	34.97	35.20	35.76	37.77	43.95	92.24	262.04
	obsd. − calcd.	−0.33	−0.29	+0.01	+0.32	−0.13						
225	obsd.	28.74	36.27	41.13	44.47	47.16	50.03	54.08	61.01	74.06	143.55	347.34
	obsd. − calcd.	−0.23	−0.14	+0.14	+0.27	−0.50						
250	obsd.	31.67	41.22	48.32	54.06	59.40	65.38	73.32	85.55	105.27	195.42	
	obsd. − calcd.	−0.21	−0.11	+0.12	+0.18	−0.51						
275	obsd.	34.55	46.04	55.32	63.53	71.66	80.98	93.09	110.47	137.31	247.45	
	obsd. − calcd.	−0.22	−0.16	+0.02	+0.13	−0.26						
300	obsd.	37.37	50.76	62.25	72.93	83.96	96.72	113.05	135.93	169.46	298.81	
	obsd. − calcd.	−0.27	−0.27	−0.07	+0.16	+0.24						
Average deviation, atm.		0.25	0.19	0.07	0.21	0.33						
Average % deviation		0.82	0.49	0.15	0.46	0.59						

Total average deviation, 0.21 atm. Total average % deviation, 0.50

Two of the isotherms studied by Rose-Innes and Young, 200 and 250°, were smoothed to our even densities: 2.5 to 5.0 moles per liter at 200°,

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(1) J. Rose-Innes and S. Young, *Phil. Mag.*, **47**, 353 (1899).

(2) B. H. Sage and W. N. Lacey, *Ind. Eng. Chem.*, **34**, 730 (1942).

(3) J. A. Beattie, *Proc. Am. Acad. Arts and Sci.*, **69**, 389 (1934).

(4) For the last reports on this work see J. A. Beattie, S. Marple, Jr., and D. G. Edwards, *J. Chem. Phys.*, **18**, 127 (1950); J. A. Beattie and S. Marple, Jr., THIS JOURNAL, **72**, 4143 (1950).

(5) J. A. Beattie, S. W. Levine and D. R. Douslin, *ibid.*, **73**, 4431 (1951).

and 2.5 to 4.0 moles per liter at 250°. Their pressures were uniformly lower than ours by an average of 1.8%.

We also made a comparison of the observations of Sage and Lacey at the densities 5, 6 and 7 moles per liter and at their temperatures 400 and 460°F. The agreement was good. At the lower temperature their pressures were higher than ours by +0.49, −0.22 and +0.55%; while at the higher temperatures the deviations were +0.57, +0.31 and +0.05%.

The second virial coefficient B_V in the equation

$$pV = RT\left(1 + \frac{B_V}{V} + \frac{C_V}{V} + \ldots\right)$$

was determined graphically at each temperature from plots of $V[(pV/RT) - 1]$ against $1/V$. These values are shown in Table III.

TABLE III

SECOND VIRIAL COEFFICIENTS OF NORMAL PENTANE

$$B_V = \text{Limit } \frac{1}{V} \longrightarrow 0\ V\left(\frac{pV}{RT} - 1\right)$$

Temp., °C.	200	225	250	275	300
B_v, l./mole	−0.405	−0.350	−0.311	−0.274	−0.244

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CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, CATHOLIC UNIVERSITY]

Sorption of Ammonia by Silk Fibroin

BY PATRICIA A. MARSHALL[1] AND WALTER J. MOORE

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The sorpion of ammonia by silk fibroin has been measured at −77 and −63°. There is a marked hysteresis in the sorption isotherms, the loop closing at zero pressure. The B.E.T. monolayer point for adsorption occurs when one ammonia molecule is held for every two peptide links in the adsorbent, whereas the monolayer point on desorption occurs at one ammonia per peptide link. Analysis of the hysteresis loop suggests that the dissipative process is due in part to viscous retardation of the swelling of the fiber, and in part to a shifting of sorbed molecules to new sites of lower energy that are exposed as a result of the swelling.

The interesting thermodynamic problems presented by a system that is completely reproducible yet completely surrounded by irreversibility have been discussed in a recent paper by Bridgman.[2] Examples occur in the stress–strain loops of plastically deformed solids, and in the metastable states produced by quenching alloys subject to order–disorder transitions. Another noteworthy example is to be found in the hysteresis of sorption isotherms. We shall describe in this paper a study of the system ammonia–silk fibroin, at −77 and −63°, in which the phenomenological aspects of the sorption hysteresis are especially clear. Previous work with polar gases on fibrous proteins is exemplified by the water–silk system at 25°,[3] though, probably owing to the higher temperature, the irreversible effects were much less evident in this case. Also, in a recent paper, Benson and Seehof[4] report evidence of hysteresis in the ammonia–egg albumin system.

Experimental Details

Raw silk was degummed by the procedure of Sookne and Harris[5] to remove the sericin from the fibroin, and dried under vacuum at 25° to constant weight. The ammonia, of 99.5% stated purity, was freed from condensable gases by repeated pumping under high vacuum, with intermittent thawing. It was stored in a sodium coated bulb.

The sorption apparatus was of the volumetric type[6] with mercury cut-off valves instead of stopcocks. Pressures were read with a cathetometer to 0.05 mm. from a wide bore mercury manometer. A fibroin sample of about 20 mg. was used. The sample tube was surrounded by a low temperature thermostat that maintained temperatures constant within ±0.2° over periods of a month or more.

Before a sorption run, a new fibroin sample was pumped at 70° and 10^{-6} mm. for 24 hours; samples previously exposed to ammonia were restored to their original condition by pumping at 70° and 10^{-6} mm. for 72 hours. Dead space volumes were determined with helium. The ammonia vapor pressures were taken from the Landolt-Börnstein Tables.

After admission of a charge of ammonia to the fibroin, adsorption was followed by the decrease in pressure, and the "equilibrium value" was defined by a change in pressure of less than 0.02 mm. per hour, corresponding to from 10^{-4} to 5×10^{-4} mole NH_3 per gram of fibroin per day. The sorption at different pressures was followed by changing the volume of the system stepwise, with the addition of more ammonia as needed. The approximate times t_e required to reach equilibrium at different relative pressures $a = p/p_0$ and temperatures T, were as follows: (1) $T = -77°$, $a > 0.22$, $t_e = 50$ hours for both adsorption and desorption; (2) $T = -77°$, $a < 0.22$, $t_e = 50$ hours on adsorption, 72 hours on desorption; (3) $T = -63°$, $a > 0.9$, $t_e = 24$ hours; (4) $T = -63°$, $a = 0.2$ to 0.9, $t_e = 50$ hours for both adsorption and desorption; (5) $T = -63°$, $a < 0.2$, $t_e = 100$ hours for adsorption and t_e for desorption increased from 96 to 144 hours with successively lower a. As a rule about 80% of the total adsorption or desorption occurred during the first half of the time, t_e.

Description of the Isotherms

The experimental isotherms are shown in Fig. 1 (−77°) and Fig. 2 (−63°). At this point it is necessary to define the *main adsorption and desorption curves*. An example of each of these is shown in the −63° isotherm, the main adsorption and desorption curves being, respectively, the lower and upper bounding curves. They were obtained by exposing the initially "dry" fibroin to ammonia atmospheres of increasing relative pressure up to a maximum of 0.99, and then desorbing from this maximum pressure to the lowest pressure measurable. At −77° the desorption was started at $a = 0.93$; hence the upper bounding curve at this temperature is not the main desorption curve, which

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[1] Abstracted from a portion of the dissertation submitted by Patricia A. Marshall in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] P. W. Bridgman, *Rev. Modern Phys.*, **22**, 56 (1950).

[3] A. C. Goodings and L. H. Turl, *J. Textile Inst.*, **31**, T69 (1940).

[4] S. W. Benson and J. M. Seehof, THIS JOURNAL, **73**, 5053 (1951).

[5] A. M. Sookne and M. Harris, *J. Research Natl. Bureau Standards*, **23**, 303 (1939).

[6] H. Frey and W. J. Moore, THIS JOURNAL, **70**, 3644 (1948).