

CADET \_\_\_\_\_ SECTION \_\_\_\_\_ TIME OF DEPARTURE \_\_\_\_\_

DEPARTMENT OF CHEMISTRY & LIFE SCIENCE

CH365 2022-2023

Beer Day Bonus

28 September 2022

TEXT: Smith, Van Ness, Abbott & Swihart

SCOPE: Lessons 10-15

TIME: 60 minutes

References Permitted: Open notes, book, internet, CHEMCAD, Mathematica, Excel.

**INSTRUCTIONS**

1. This is a BONUS exercise and is due **1630 7 October 2022**.
2. There are 2 problems on 1 page in this exercise (not including the cover page).
3. Save all electronic work to your SharePoint Directory.
4. Write down the file name and file location.

(TOTAL WEIGHT: 50 POINTS)

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DO NOT WRITE IN THIS SPACE

PROBLEM	VALUE	CUT
A	40	
B	10	
TOTAL BONUS	50	

Problem:    Weight:  
A                40

Table I in the attached paper contains experimental calculated pressures of xenon gas as a function of temperature and molar density. In the same table, directly under the measured values, calculated values of pressure are shown as deviations from the measurements. The calculations were performed with the Beattie-Bridgeman equation of state, which is presented in Table II in the paper along with the constants used in the equation. The assignment is to repeat the calculations in the table using the Beattie-Bridgeman equation. A spreadsheet accompanies this handout with the experimental values typed in, in the same format at Table I. Complete the green-shaded cells in the accompanying spreadsheet.

Problem:    Weight:  
B                10

Calculate the average deviation, average percent deviation, total average deviation, and total average percent deviation for your results. Complete the yellow-shaded cells in the accompanying spreadsheet.

# The Compressibility of Gaseous Xenon. I. An Equation of State for Xenon and the Weight of a Liter of Xenon

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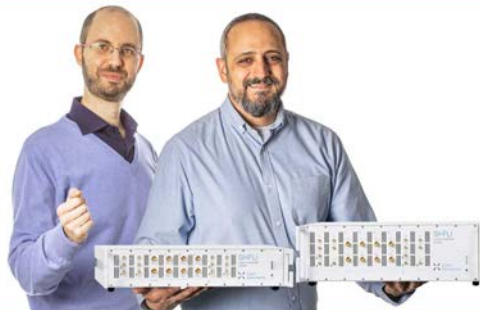
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## The Compressibility of Gaseous Xenon. I. An Equation of State for Xenon and the Weight of a Liter of Xenon

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(Received June 4, 1951)

The compressibility of xenon containing 0.14 mole percent of krypton has been measured from 16.65° (the critical temperature) to 300°C and over the density range 1 to 10 mole per liter. The constants of the Beattie-Bridgeman equation of state for the sample used and for pure xenon have been determined from these measurements. The constants for pure xenon are  $R=0.08206$ ,  $A_0=4.6715$ ,  $a=0.03311$ ,  $B_0=0.07503$ ,  $b=0$ ,  $c=30.02\times 10^4$  in units of normal atmos, liter per mole, and °K ( $T^\circ\text{K}=t^\circ\text{C}+273.13$ ). The weight of one liter of Xe at a pressure of one standard atmosphere is calculated from its molecular weight (131.3) and the above parameters to be 5.897 g per liter at 0°C and 5.467 g per liter at 70°F.

RECENTLY the noble gases have become available in quantity and in a state of high purity. When the present investigation of the compressibility of xenon was begun the details of final purification and especially of accurate analysis had not been worked out to as successful conclusion as at the present time. However the xenon used in the present investigation contained far less impurity than any heretofore available.

Ramsay and Travers<sup>1</sup> studied the compressibility of Xe at 11.2°C to 50 atmos and at 237.3°C to 100 atmos. The present measurements were made on a sample of Xe containing 0.14 mole percent Kr and cover the temperature range 16.65° (the critical temperature) to 300°C and the density range 1 to 10 mole per liter, the maximum pressure being 406 atmos.

We are greatly indebted to Dr. John M. Gaines, Dr. Roger H. Gillette, and the Linde Air Products Company for the gift of the sample of Xe used in the present investigation, and to the Linde Air Products Company for a grant-in-aid that made the work possible.

The procedure for controlling the temperature and density of the gas and the method of measuring mass, volume, pressure, and temperature have been described elsewhere<sup>2</sup> and are the same as those employed for the study of the compressibilities of a number of hydro-

carbons and their mixtures.<sup>3</sup> For the measurements on Xe the all-steel bomb having a volume of about 200 ml was used.

In our procedure we inject sufficient mercury into the bomb holding the gas so that at each temperature the pressures are read for the same molar density of gas. This compressor setting depends then on the mass of gas in the bomb and its molecular weight. The latter is affected by the purity of the gas. The sample of Xe used in the present work weighed 22.28615 grams. The measurements were completed on the assumption that the gas was pure Xe and had a molecular weight of 131.3. When  $B(V, T)$  defined by the relation,

$$B(V, T) = V(pV - RT),$$

was plotted at each temperature against molar density ( $1/V$ ) the curves for xenon (and to a greater extent those for krypton) did not approach linearity as the density approached zero. This indicated an error in  $RT$  or in  $V$ , the molar volumes used. Since  $RT$  was calculated for the absolute thermodynamic (not the International) temperature scale we suspected the molecular weight used. This could be in error because of an incorrect atomic weight for Xe, or because of an impurity in the gas.

In the meantime Dr. Gillette made an analysis of the gas in one of the unused ampules on a mass spectrometer

<sup>1</sup> W. Ramsay and M. W. Travers, *Phil. Trans. Royal Soc. (London)*, **A197**, 47 (1901).

<sup>2</sup> J. A. Beattie, *Proc. Am. Acad. Arts and Sci.* **69**, 389 (1934).

<sup>3</sup> For the last reports on this work see Beattie, Marple, Jr., Edwards, *J. Chem. Phys.* **18**, 127 (1950); J. A. Beattie and S. Marple, Jr., *J. Am. Chem. Soc.* **72**, 4143 (1950).

TABLE I. Comparison of the pressures calculated from the equation of state with the observed pressures for gaseous xenon.

(For each temperature the first line gives the observed pressure and the second line gives the observed pressure minus the pressure calculated from the equation given in Table II. The critical constants of xenon are approximately:  $t_c = 16.65^\circ\text{C}$ ,  $p_c = 57.89$  atmos,  $d_c = 8.32$  mole per liter.)

Density, mole/liter	1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5	5.0	6.0	7.0	8.0	9.0	10.0
Temp., $^\circ\text{C}$ (Int.)	Pressure, standard atmosphere													
16.65 obsd.	20.667	28.817	35.652	41.292	45.853	49.467	52.224	54.226	55.720	57.29	57.78	57.88	57.91	58.02
obsd.-calc.	-0.067	-0.150	-0.257	-0.367	-0.465	-0.518	-0.534	-0.472	-0.303	0.38	1.57	3.16	4.67	5.46
25 obsd.	21.443	30.040	37.366	43.537	48.670	52.872	56.282	59.000	61.140	64.12	65.97	67.32	68.60	70.38
obsd.-calc.	-0.045	-0.111	-0.193	-0.277	-0.345	-0.391	-0.376	-0.300	-0.151	0.40	1.23	2.17	2.83	3.00
50 obsd.	23.731	33.652	42.418	50.131	56.909	62.864	68.086	72.691	76.776	83.79	89.82	95.58	101.69	109.39
obsd.-calc.	-0.007	-0.025	-0.049	-0.079	-0.099	-0.101	-0.097	-0.073	-0.035	0.07	0.11	-0.05	-0.59	-1.10
75 obsd.	26.007	37.223	47.387	56.619	64.959	72.575	79.550	85.989	91.970	103.01	113.41	123.93	135.57	149.13
obsd.-calc.	0.029	0.041	0.051	0.076	0.051	0.040	0.020	-0.007	-0.067	-0.26	-0.64	-1.30	-2.07	-2.98
100 obsd.	28.268	40.759	52.290	62.957	72.880	82.128	90.837	99.071	106.952	122.03	136.87	152.36	169.60	189.82
obsd.-calc.	0.056	0.087	0.115	0.129	0.143	0.121	0.092	0.015	-0.094	-0.46	-1.05	-1.82	-2.53	-2.79
125 obsd.	30.512	44.262	57.152	69.262	80.702	91.573	101.983	112.008	121.753	140.87	160.19	180.76	203.63	230.35
obsd.-calc.	0.072	0.113	0.159	0.186	0.189	0.168	0.303	0.022	-0.136	-0.59	-1.23	-1.89	-2.35	-1.93
150 obsd.	32.741	47.744	61.973	75.505	88.460	100.918	113.000	124.814	136.446	159.60	183.45	208.98	237.61	270.92
obsd.-calc.	0.076	0.127	0.180	0.204	0.211	0.173	0.102	-0.001	-0.160	-0.64	-1.21	-1.75	-1.71	-0.38
175 obsd.	34.967	51.211	66.754	81.710	96.150	110.161	123.943	137.533	151.014	178.22	206.49	237.25	271.61	311.41
obsd.-calc.	0.081	0.133	0.174	0.208	0.197	0.120	0.067	-0.034	-0.208	-0.64	-1.18	-1.27	-0.66	1.60
200 obsd.	37.194	54.673	71.552	87.883	103.838	119.458	134.892	150.195	165.564	196.78	229.62	265.35	305.38	351.84
obsd.-calc.	0.089	0.140	0.196	0.197	0.207	0.157	0.086	-0.061	-0.196	-0.59	-0.89	-0.72	0.47	3.92
225 obsd.	39.412	58.127	76.308	94.056	111.473	128.683	145.733	162.810	179.984	215.23	252.54	293.30	338.70	391.86
obsd.-calc.	0.090	0.144	0.184	0.200	0.184	0.150	0.035	-0.085	-0.250	-0.55	-0.68	-0.13	1.40	6.16
250 obsd.	41.637	61.584	81.082	100.208	119.118	137.871	156.634	175.428	194.476	233.74	275.57	321.39	372.92	
obsd.-calc.	0.099	0.154	0.196	0.193	0.188	0.130	0.076	-0.065	-0.180	-0.37	-0.24	0.76	3.44	
275 obsd.	43.860	65.026	85.825	106.346	126.709	147.015	167.371	187.963	208.811	252.06	298.51	349.18	406.15	
obsd.-calc.	0.108	0.153	0.184	0.181	0.151	0.085	-0.022	-0.095	-0.225	-0.32	0.20	1.46	4.66	
300 obsd.	46.057	68.457	90.557	112.456	134.290	156.129	178.146	200.418	223.184	270.43	321.16	377.08		
obsd.-calc.	0.092	0.143	0.166	0.148	0.116	0.026	-0.060	-0.176	-0.196	-0.16	0.43	2.39		
Av. dev. (atmos)	0.070	0.117	0.162	0.188	0.196	0.168	0.144	0.108	0.169	0.42	0.82	1.45	2.28	2.93
Av. percent dev.	0.21	0.25	0.28	0.29	0.28	0.23	0.20	0.14	0.15	0.31	0.69	1.15	1.71	2.23

Total average deviation (atmos), 0.611; total average percent deviation, 0.546.

Total average deviation (atmos) from 1 to 8 mole/liter, 0.334; total average percent deviation from 1 to 8 mole/liter, 0.349.

and found that the sample of Xe contained 0.105 mole percent Kr but Ne, Ar, O<sub>2</sub>, and N<sub>2</sub> were not detected although looked for. At this time we were using 83.8 as the molecular weight of Kr since we believed that the atomic weight of Kr was too small by 0.1 unit. This gave 131.250 ( $= 0.99895 \times 131.3 + 0.00105 \times 83.8$ ) for the average molecular weight of the sample, a difference of 0.050 from the value used in computing the mercury compressor settings to give integer and half-integer gas densities in the bomb. Subsequently a second analysis of a sample of the gas actually used in the compressibility runs was found by Dr. Gillette to contain  $0.14 \pm 0.01$  mole percent Kr. If we use the accepted atomic weight for Kr, 83.7, we find the molecular weight of the sample of Xe to be 131.233 ( $= 0.9986 \times 131.3 + 0.0014 \times 83.7$ ). The accepted atomic weight of Kr is used here since the measurements of the compressibility

of Kr were reasonably well correlated on this basis, the earlier discrepancies in the values of  $B(V, T)$  for Kr being explained by the presence of some Xe.

The original pressures were measured for gas densities computed on the basis of a molecular weight of 131.3 for Xe. From these a value of  $B(V, T)$  was computed for each point the corresponding molar volume being computed on a basis of a molecular weight of 131.250 for the gas in the bomb, that is, each density was multiplied by the factor  $131.3/131.250 = 1.00038095$ . The values of  $B(V, T)$  corresponding to integer and half-integer densities at each temperature were then obtained by interpolation without smoothing. This was possible since the change in any one density was only 0.038 percent. The pressures so obtained are listed in Table I.

On the basis of the latest analysis the molecular

TABLE II. Constants of the Beattie-Bridgeman equation of state for xenon.

Composition in mole percent	$p = [RT(1 - \epsilon)/V^2] [V + B] - A/V^2$ $B = B_0(1 - b/V)$ $\epsilon = c/VT^3$						Molecular weight
	Units: standard atmosphere, liter per mole, °K (°K = t°C + 273.13)						
	$R$	$A_0$	$a$	$B_0$	$b$	$c$	
99.86 percent Xe, 0.14 percent Kr	0.08206	4.6678	0.03310	0.07500	0	$30.00 \times 10^4$	...
100 percent Xe	0.08206	4.6715	0.03311	0.07503	0	$30.02 \times 10^4$	131.3

weight of the sample was 131.233 which would change each density by 0.013 percent and the corresponding pressure from 0.01 percent to 0.02 percent at a maximum. This is well within the accuracy of the measurements which may be placed in the range 0.05 percent to 0.10 percent.

The constants of the Beattie-Bridgeman equation of state for the mixture are given in Table II. We used the value 273.13 for the Kelvin temperature of the ice point for the purpose of fitting the equation to the measurements because it has been used for all of the other gases to which the equation has been applied. From these equation of state constants, the final analysis of the mixture, and the constants for krypton<sup>4</sup> we computed the constants for pure Xe from the relations<sup>5</sup>

$$\begin{aligned}
 A_{0m} &= (x_1 A_{01}^{\frac{1}{2}} + x_2 A_{02}^{\frac{1}{2}})^2 \\
 B_{0m} &= \frac{1}{4} (x_1 B_{01} + x_2 B_{02}) \\
 &\quad + \frac{3}{4} (x_1 B_{01}^{\frac{1}{2}} + x_2 B_{02}^{\frac{1}{2}}) (x_1 B_{01}^{\frac{1}{2}} + x_2 B_{02}^{\frac{1}{2}}) \quad (1) \\
 c_m &= (x_1 c_1^{\frac{1}{2}} + x_2 c_2^{\frac{1}{2}})^2 \\
 a_m &= x_1 a_1 + x_2 a_2 \\
 b_m &= x_1 b_1 + x_2 b_2,
 \end{aligned}$$

where the subscripts  $m$ , 1, 2 denote the mixture, Xe, Kr, respectively; and  $x$  is the mole fraction of a constituent. The constants for pure Xe are also listed in Table I. In this computation we took  $x_1 = 0.9986$  and  $x_2 = 0.0014$ , the values given by the latest analysis of the gas sample.

#### WEIGHT OF A LITER OF XENON AT ONE ATMOSPHERE PRESSURE

The results of the calculation of the weight of one liter of Xe under a pressure of one standard atmosphere at 0°C and at 70°F are given in Table III. The molar

volume  $V$  at 1 atmos was computed from the equation

$$\begin{aligned}
 V &= RT + \beta/V + \gamma/V^2 \quad (p = 1 \text{ atmos}), \quad (2) \\
 \beta &= RTB_0 - A_0 - Rc/T^2, \\
 \gamma &= A_0 a - RB_0 c/T^2,
 \end{aligned}$$

the virial coefficients being evaluated from the values of the constants listed in Table I. Two separate calculations were made. One was based on  $RT$  and  $T_0$  obtained from  $R = 0.08206$  and  $T_0 = 273.13$ . In the second the same values of the virial constants were used but the leading term  $RT$  was evaluated from Birge's<sup>6</sup> value

TABLE III. Weight of one liter of xenon at a pressure of one standard atmosphere.

See Eq. (2)	$\beta$ atmos.- l <sup>2</sup> /mole <sup>2</sup>	$\gamma$ atmos.- l <sup>3</sup> /mole <sup>3</sup>	$V^a$ liter/mole	$m^a$ g/liter	$V^b$ liter/mole	$m^b$ g/liter
			$t = 0^{\circ}\text{C}$			
-3.3201	+0.130		22.2642	5.897	22.2652	5.897
			$t = 70^{\circ}\text{F}$			
-3.1444	+0.133		24.0147	5.467	24.0150	5.467

Molecular weight of Xe = 131.3 g/mole.

<sup>a</sup> Based on  $RT = 22.4130$  at 0°C and  $RT = 22.4154$  at 70°F.

<sup>b</sup> Based on  $RT = 22.4140$  at 0°C and  $RT = 24.1457$  at 70°F.

$RT_0 = 22.4140$  liter-atmos per mole and the Kelvin temperature derived from the work of this laboratory

$$\begin{aligned}
 T^{\circ}\text{K} &= 273.16 + t + (t/100)(t/100 - 1)(0.04217 \\
 &\quad - 7.481 \times 10^{-8}t), \quad t = t^{\circ}\text{C (Int)} \\
 &\quad 0^{\circ} < t < 450^{\circ}\text{C}
 \end{aligned}$$

and mentioned by Stimson<sup>7</sup> in his report on the International Temperature Scale of 1948. The two values of the weight of a liter agree to  $3 \times 10^{-4}$  g at 0° and  $1 \times 10^{-4}$  g at 70°F.

<sup>6</sup> R. T. Birge, Revs. Modern Phys. **13**, 233 (1941).

<sup>7</sup> H. F. Stimson, J. Research Natl. Bur. Standards **42**, 209 (1949).

<sup>4</sup> Beattie, Brierley, and Barriault, to be published.

<sup>5</sup> See J. A. Beattie, Chem. Phys. **44**, 141 (1949).