Compressibility and Vapor Pressure of Methyl Borate

RICHARD G. GRISKEY, WALTER E. GORGAS, and LAWRENCE N. CANJAR

Carnegie Institute of Technology, Pittsburgh, Pennsylvania

Pressure-volume-temperature measurements have been made on methyl borate over the temperature range of 225° to 300°C. and pressures of 30 to 200 atm. in a variable volume *P-V-T* bomb. Vapor-pressure measurements from 180°C. to the critical point have also been made with the same apparatus. The vapor-pressure data are presented in the form of the Antoine equation, and the *P-V-T* data together with the vapor-pressure data have been fitted to the Benedict-Webb-Rubin equation of state.

With exception of vapor-pressure measurements made by Webster and Dennis (*7*) and the vapor-pressure and orthaboric-density measurements of Hansen and Hughes (*4*), no previous work has been done on the *P-V-T* properties of methyl borate.

The apparatus used in this investigation is a modification of the design of Keyes (*5*) and Beattie (*1*). Except for certain changes which have been described by Li and Canjar (*6*), a detailed description of the equipment was published by Cherney, Marchman, and York (*3*). The methyl-borate sample was prepared from special-grade (99.9% pure) material. After a portion of the stock had been distilled in the presence of sodium in a closed system, the middle third of the distillate was frozen, exposed to vacuum, liquefied, frozen again, exposed to vacuum, liquefied again, and sealed in a glass ampule.

It was discovered that methyl borate over mercury slowly decomposed with time, particularly at high temperatures. In order to minimize the effect of this decomposition, the data were obtained as rapidly as possible in two sets. The vapor-pressure runs were made over the temperature range of 180° to 230°C. The initial pressure measured at 180°C. was 16.722 atm. After all the vapor-pressure measurements had been made, a repeat measurement was made at 180°C., and a pressure of 16.950 atm. was obtained. Normally when these measurements are made on other compounds, the difference in the pressure of the initial measurement and the repeat measurement is negligible, indicating no chemical change. In this work the decomposition effect was appreciable.

A second set of runs was made to determine the compressibility of gaseous methyl borate in the temperature range of 225° to 300°C. One of the first measurements made at a density of 1.545 moles/liter and 300°C. gave a pressure of 49.616 atm. After all the data in this set of runs had been obtained, this same point was remeasured, and the pressure was found to be 49.749 atm., again an indication of a decomposition effect.

The uncertainty in vapor-pressure determinations is much larger. When measurements are made in the two-phase region, the pressure of a pure component remains constant when the volume is varied over an isotherm. Because of the presence of decomposition products in the methyl-borate sample, the pressure changed as vaporization took place at constant temperature. This made the exact location of the critical point impossible and added another uncertainty in the actual value of the vapor pressure. The uncertainty is a maximum at the critical point and is estimated to be 0.5 atm.

The vapor pressure data, given in Table 1, can be represented by the Antoine equation:

$$\log_{10} p_{\text{atm.}} = 4.18470 - \frac{1164.0}{T\text{-}60}$$

where T is temperature in °K

Residuals of observed pressures minus calculated pressures are given in Figure 1.

A summary of the *P-V-T* properties of gaseous methyl borate is given in Table 2. These data and the vapor-pressure data have been fitted to the Benedict-Webb-Rubin equation (*2*):

$$P = RTd + \left(BoRT - Ao - \frac{Co}{T^2}\right)d^2 + (bRT - a)d^3 + \alpha Rd^6 + \left(\frac{Cd^3}{T^2}\right)\left(1 + \gamma d^2\right)e^{-\lambda d^2}$$

where $Ao = -31.589$, $Bo = -0.4332$, $Co = 7.363 \times 10^6$, $a = 23.272$, $b = 0.3417$, $c = 2.790 \times 10^6$, $\alpha = 7.8 \times 10^{-4}$, $\gamma = 0.033$, R = 0.0820567 when P is given in atm., T in °K., and d in g.-moles/liter. The average percentage deviation between observed pressures and pressures calculated from the Ben-

Table 1. Vapor Pressure of Methyl Borate

Temperatures, °C.	Vapor pressure, atm.
180.00	16.72
202.16	24.12
209.79	27.11
220.00	31.44

Table 2. Compressibility Measurements of Methyl Borate

Temperature, °C.	Density, g. moles/liter	Pressure, atm.
225	1.545	32.53
	1.943	34.26
	2.632	35.20
	3.248	35.64
	3.561	35.91
	3.805	36.08
	4.244	37.72
	4.489	39.49
	4.809	44.87
	5.244	60.66
	5.582	85.83
	6.367	211.56
—	—	—
250	1.117	34.16
	1.550	38.32
	1.790	40.79
	1.948	42.21
	2.174	43.90
	2.438	45.79
	2.848	48.00
	3.356	51.16
	4.102	59.02
	4.556	69.51
	4.943	85.34
	5.253	105.87
	5.463	131.02
	5.709	156.16
	5.862	181.68
	6.018	211.49
—	—	—
275	1.238	38.45
	1.554	44.07
	1.793	47.84
	2.585	57.99
	3.023	63.14
	3.488	69.79
	4.139	84.01
	4.658	104.79
	4.958	123.89
	5.309	156.09
	5.545	186.26
	5.701	211.41
—	—	—
300	1.236	42.63
	1.545	49.61
	1.795	54.72
	2.133	61.06
	2.745	67.19
	2.836	73.74
	3.383	85.55
	3.873	99.63
	4.321	118.73
	4.853	154.92
	5.157	186.13
	5.342	211.27
	1.545(recheck)	49.74

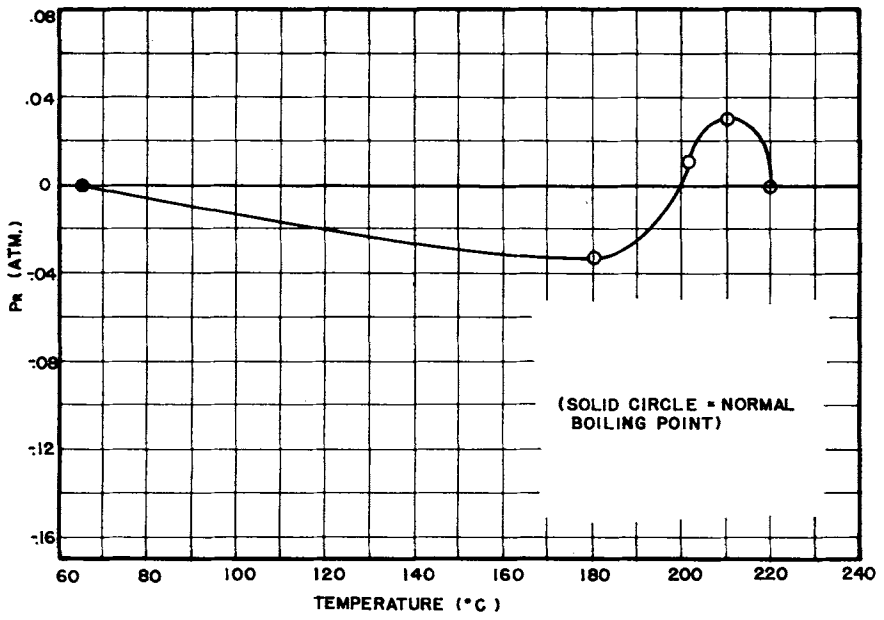

Fig. 1. Vapor pressure residual P_R vs. temperature.

edict-Webb-Ruben equation of state is 0.64%.

The critical temperature is estimated to be 228.5° ± 0.5°C. and the critical pressure 35.4 ± 0.5 atm.

ACKNOWLEDGMENT

This research was supported by the Callery Chemical Company. Grateful acknowledgment is hereby made.

LITERATURE CITED

1. Beattie, J. A., *Proc. Am. Acad. Arts Sci.*, **69**, 589 (1934).
2. Benedict, Manson, G. B. Webb, and L. C. Rubin, *J. Chem. Phys.*, **8**, 334 (1940).
3. Cherney, B. J., Henry Marchman, and Robert York, *Ind. Eng. Chem.*, **41**, 2653 (1949).
4. Hansen, C. E., and R. L. Hughes, *A.I.Ch.E. Journal*, to be published.
5. Keyes, F. G., *Proc. Am. Acad. Arts Sci.*, **68**, 505 (1933).
6. Li, Kun, and L. N. Canjar, *Chem. Eng. Progr. Symposium Series No. 7*, **49**, 147 (1953).
7. Webster, S. H., and L. M. Dennis, *J. Am. Chem. Soc.*, **55**, 3233 (1933).

Manuscript received June 25, 1959; revision received August 5, 1959; paper accepted August 10, 1959.

The Motion of Two Spheres Following Each Other in a Viscous Fluid

JOHN HAPPEL and ROBERT PFEFFER

New York University, New York, New York

The purpose of this investigation was to determine the interaction effect of one spherical particle upon another when both are falling in a viscous fluid. The velocities of two identical spheres, falling along the axis of a cylinder in a direction parallel to their line of centers, were measured experimentally as a function of the center-to-center distance between them at very low Reynolds numbers. The experimental results compared very well with theoretical studies found in the literature which predicted that two spheres will fall faster than one sphere.

At Reynolds numbers greater than 0.25 the influence of inertial effects were studied for one and two spheres. The experimental results qualitatively confirmed the Oseen equations. A definite attraction between two spheres falling one above the other was observed; the inertial forces acted to slow down the lower sphere without affecting the upper one.

The behavior of spherical particles settling in a viscous fluid is of fundamental importance in solving problems involving sedimentation, flow through packed beds, and fluidization. However both mathematical analysis and experimental observation are extremely difficult when dealing with assemblages of particles because of the many boundary conditions and interaction effects encountered. In addition to these complications, as soon as the particle Reynolds number becomes as high as 0.25, the inertial terms can no longer be neglected in the solution of the Navier-Stokes equations of motion.

For these reasons a logical start in attempting to solve problems involving many particles is to carry out a complete study of the important variables affecting the motion of one particle at very low Reynolds numbers. Then these observations can be used to study the motion of two particles and so on, until eventually enough theoretical and experimental information is available to predict the motion of the complex particle systems actually encountered in practice. The same technique can be utilized in studying the inertial effects which become important at higher Reynolds numbers.

The purpose of the investigation described in this paper was to continue to add to the information available concerning the motion of two particles settling one above the other in a viscous fluid. As an idealization of the numerous particle shapes conceivable, identical, smooth, and rigid spheres were chosen to work with.

Experimental measurements were made at low Reynolds numbers (much less than 0.25) of two spheres settling along the axis of a cylindrical tube in a direction parallel to their line of centers. This was done to determine how well the theoretical equations of motion, and the pertinent correction factors which take into account the boundary and interaction effects, could predict the actual motion. The influence of inertial effects at higher Reynolds numbers on the motion of two spheres was also determined experimentally and compared with the corresponding effects on a single sphere. A qualitative analysis of the motion of three spheres will also be discussed.

DESCRIPTION OF APPARATUS

The apparatus used for taking velocity measurements consisted of a cylindrical Pyrex glass column 32 in. long with an