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## The Pressure-Volume-Temperature Relations for Gaseous Monomethylamine<sup>1</sup>

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### Introduction

The possible and probable use of monomethylamine as the refrigerating fluid in the absorption type of refrigerating units has led to the determination of its thermodynamic properties in this Laboratory.<sup>2</sup> Since the chemical literature records no systematic investigation of the pressure-volume-temperature relations, such determinations constituted the experimental object of this study.

Leduc<sup>3</sup> has proposed an equation of state for monomethylamine, based *not* upon  $p$ - $v$ - $T$  relations, but derived by aid of the theory of corresponding states. Mehl<sup>4</sup> has proposed an equation of state of the Callendar-Mollier type based upon a knowledge of some specific gas volumes and of the heat-capacity ratio.

In this investigation an equation of state will be fitted to the observed  $p$ - $v$ - $T$  data.

**The Proposed Method.**—The method adopted for this investigation is the one that has been in common usage at the Research Laboratory of Physical Chemistry at the Massachusetts Institute of Technology, and which has been described in numerous papers.<sup>5</sup> The method, in essentials, consists of determining the pressures developed by a given mass of substance at different temperatures, the volume being held constant. Thus is obtained a series of pressure-temperature relations at different specific volumes.

From the experimental data thus obtained, an equation of state of the Keyes type<sup>6</sup> was derived; this relation reproduces the experimental values with satisfactory accuracy.

(1) Constructed from a thesis presented to the Graduate Faculty of The University of Texas by Charles T. Kenner in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1939. Present address (C. T. K.): The Citadel, The Military College of South Carolina, Charleston.

(2) (a) Felsing and Thomas, *Ind. Eng. Chem.*, **21**, 1269 (1929); (b) Felsing and Wohlford, *THIS JOURNAL*, **54**, 1442 (1932); (c) Felsing and Buckley, *J. Phys. Chem.*, **37**, 779 (1932); (d) Felsing and Jessen, *THIS JOURNAL*, **55**, 447 (1933); (e) Felsing and Ashby, *ibid.*, **56**, 2226 (1934).

(3) Leduc, *Compt. rend.*, **148**, 407, 549 (1909).

(4) Mehl, *Beihfte. Z. für gesamte Kälte-Ind.*, No. 3, p. 27 (1933).

(5) (a) Keyes and Brownlee, "Thermodynamic Properties of Ammonia," John Wiley and Sons, Inc., New York, 1916, p. 11; (b) Keyes and Felsing, *THIS JOURNAL*, **41**, 589 (1919); (c) Beattie and Edel, *Ann. Physik*, **11**, 633 (1931); (d) Keyes, *Proc. Am. Acad. Arts Sci.*, **68**, 505 (1933).

(6) Keyes, *Proc. Natl. Acad. Sci.*, **3**, 323 (1917).

### The Apparatus

The apparatus was a development of the dead-weight piston type pressure gage devised by Amagat and which has been thoroughly described by Keyes and Brownlee,<sup>6a</sup> Keyes and Felsing,<sup>6b</sup> and in its present form by Beattie and Edel<sup>6c</sup> and by Keyes.<sup>6d</sup> No essential differences in design of the pressure measuring device existed. The accuracy attainable in pressure measurements alone is at least 1 part in 3000 at pressures below 10 atmospheres, 1 part in 10,000 or better for pressures 10 to 20 atmospheres, and 1 part in 20,000 for pressures above 20 atmospheres.

**Temperatures** were measured by a platinum resistance thermometer, calibrated by the National Bureau of Standards, in conjunction with a calibrated Mueller bridge and a high sensitivity galvanometer. The thermometer was calibrated again during the investigation at the ice-point, at the boiling point of water, and at the boiling point of mercury. The true boiling point temperatures of water and of mercury were evaluated from the observed data by means of the relations proposed by Beattie and Blaisdell<sup>7</sup> and by Beattie, Blaisdell and Kaminsky.<sup>8</sup> Temperatures could be measured readily with an accuracy of at least 0.001°.

**The thermostat** consisted of a large Pyrex dewar flask of about 10 inches (25 cm.) internal diameter and 24 inches (61 cm.) deep. The bath liquids were liquid paraffin, Crisco, or high melting paraffin, depending upon the temperature range. The temperature of the bath could be held constant to  $\pm 0.002^\circ$  for fifteen- to twenty-minute intervals.

All necessary parts of the assembly were calibrated carefully with mercury before use. The piston was calibrated by the method of Bridgeman,<sup>9</sup> employing liquid carbon dioxide at 0°, where its vapor pressure is 26,144.7 mm. The average millimeter equivalent of 1 g. on the piston was 2,00107.

### Preparation of Material

The best c. p. Eastman Kodak Co. monomethylamine hydrochloride was dried for several hours at 110°, followed by extended drying over sulfuric acid in a desiccator. This dried hydrochloride was extracted with highly purified, dry chloroform to remove any di- and trimethylamine hydrochlorides. The extracted salt was again dried at 110° and was kept over sulfuric acid.

After evacuation of the generating and drying system,<sup>10</sup> the methylamine gas was generated by treatment of the purified hydrochloride (mixed with a small amount of yellow mercuric oxide to remove any ammonia) with a 40-50% potassium hydroxide solution. The liberated gas passed through several long drying tubes filled with potas-

(7) Beattie and Blaisdell, *Proc. Am. Acad. Arts Sci.*, **71**, 361 (1937).

(8) Beattie, Blaisdell and Kaminsky, *ibid.*, **71**, 375 (1937).

(9) Bridgeman, *THIS JOURNAL*, **49**, 1174 (1927).

(10) Felsing and Wohlford, *ibid.*, **54**, 1442 (1932).

sium hydroxide pellets into a reservoir partially filled with sodium wire and cooled by a dry-ice-acetone mixture. The liquefied amine was allowed to remain in contact with the sodium for at least eight hours until a blue color developed in the solution; this blue color was caused, most probably, by the formation of solvated sodium ions and indicated that the amine was dry. During this period the system was "flushed out" several times by opening the connection to the vacuum system for short intervals, to remove the hydrogen formed. From this reservoir the amine was condensed into an evacuated glass reservoir surrounded by dry-ice; again this system was flushed repeatedly to remove any permanent gas. The amine finally was condensed into a metal reservoir for storage.

From this storage reservoir the amine was distilled in a vacuum into a calibrated three-bulb volumeter of the form described by Keyes and Felsing.<sup>5b</sup> The loading of the piezometer also followed their procedure, except that liquid air was used as the bath surrounding the piezometer during the loading process. This procedure ensured a negligible error in determining the amount of amine left in the volumeter and in the lines of the loading apparatus because of the extremely low vapor pressure of the amine at liquid air temperatures.<sup>2a</sup>

### The Experimental Data

The experimental data, calculated to atmospheres, are presented in the table, together with the values of the pressure calculated by the

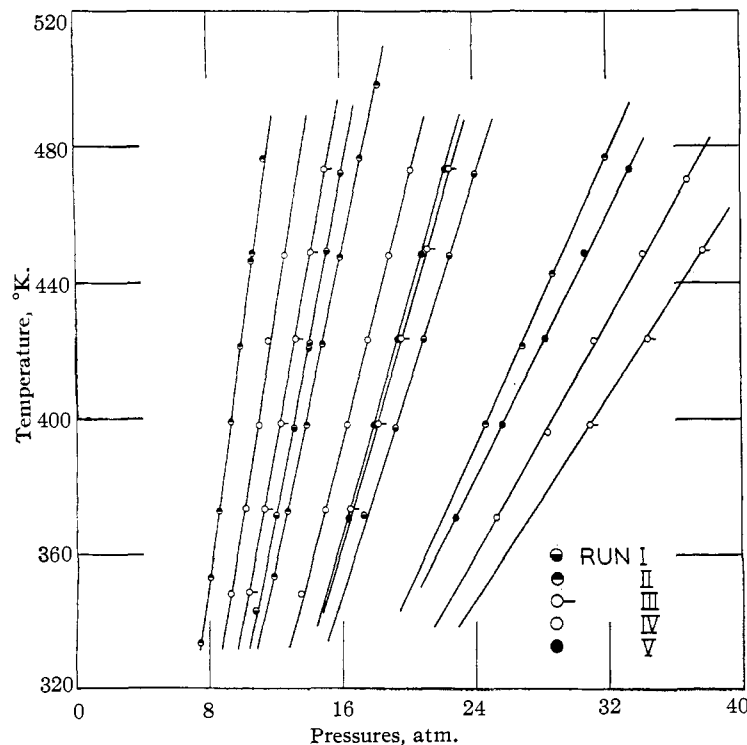


Fig. 1.—Run I, specific volumes, 74.151 and 48.115 cc.; Run II, spec. vol., 107.058, 69.726, and 35.796 cc.; Run III, spec. vol., 79.756, 51.753, and 26.583 cc.; Run IV, spec. vol., 90.253, 58.514, and 30.002 cc.; and Run V, 52.588 and 34.088 cc.

equation of state fitted to the observed data, as shown in the section following.

### Treatment of Results

The observed pressures were plotted on a large scale as functions of the temperature at the various specific volumes (see figure). The lines were linear over the entire range, though, in several runs, the first and last points seem to indicate a slight curvature. For the purpose of evaluating an equation of state, it was considered sufficiently accurate to consider these isometrics to be linear. Values of  $(\partial p/\partial T)_v$  were determined from these linear relations; these values are shown in the table.

It was decided to apply the Keyes equation<sup>6</sup> to the data of this investigation; this equation has the form

$$p = RT/(v - \delta) - A/(v - l)^2$$

where  $\delta = f(T)$  and  $A$  and  $l$  are constants characteristic of the substance. On differentiation, this equation leads to the expression

$$(\partial p/\partial T)_v = R/(v - \delta) \text{ or } \delta = v - R/(\partial p/\partial T)_v$$

The values of  $(\partial p/\partial T)_v$ , as determined for each isometric, were used to calculate values of  $\delta$ . A plot of  $\log_{10} \delta$  as a function of  $1/v$  yielded a linear relation between  $\delta$  and the volume,  $v$

$$\log_{10} \delta = 1.0548 - 6.120/v$$

which relation reproduces the observed  $\delta$  values fairly well, except at large specific volumes.

The cohesive pressure term,  $\phi$ , in the Keyes equation is

$$\phi = A/(v - l)^2 = \left( \frac{RT}{v - \delta} \right) - p$$

The values of  $\phi$  are calculated readily from values of  $\delta$  and of  $p$  at any given  $T$ . The values of  $\phi$  were calculated for each individual measurement; the average of these closely agreeing values was taken as the correct  $\phi$  for the particular specific volume. Since  $\phi = A/(v - l)^2$  and  $v = (A^{1/2}/\phi^{1/2}) + l$  a graphical representation of  $1/\phi^{1/2}$  as a function of  $v$  yielded the linear relation  $\phi = 17,940/(v + 1.759)^2$ .

The Keyes type of equation, hence, for gaseous monomethylamine becomes

$$[p + 17,940/(v + 1.759)^2][v - \delta] = RT$$

OBSERVED AND CALCULATED PRESSURES OF GASEOUS MONOMETHYLAMINE

Run	Sp. vol., cc./g.	Temp., °K.	Press., atm. Obsd.	Calcd.	(∂p/∂T) <sub>v</sub> (calcd.)									
I	74.151	343.28	10.771	10.895	0.04081	IV(b)	58.280	373.179	14.985	15.001	0.05615			
		371.78	12.071	12.058			398.327	16.397	16.347					
		371.63	12.041	12.052			90.253	348.202	9.310	9.307	.03281			
		397.08	13.125	13.090			373.763	10.200	10.145					
		420.40	14.039	14.042			398.072	11.015	10.943					
		422.18	14.137	14.115			423.099	11.837	11.764					
		449.15	15.181	15.215			448.243	12.693	12.589					
		472.13	16.108	16.153			473.224	13.404	13.409					
		48.115	371.68	17.410			17.564	.06666	58.514	348.167	13.464	13.616	.05329	
			397.18	19.241			19.261		373.742	14.970	14.978			
			423.18	20.987			20.997		398.078	16.305	16.276			
			449.05	22.561			22.721		423.147	17.636	17.611			
			472.23	24.125			24.267		448.218	18.938	18.947			
		II	107.058	333.659			7.492	7.565	.02721	30.002	373.557	25.259	25.314	.11537
				333.580			7.495	7.563		398.059	28.336	28.141		
353.081	8.059			8.094	423.066	31.147	31.026							
353.120	8.058			8.095	448.262	34.112	33.933							
372.950	8.622			8.635	473.002	36.834	36.787							
372.981	8.621			8.636	52.588	V	373.434	16.308		16.404	.06019			
398.584	9.324			9.332		398.191	17.911	17.894						
421.456	9.946			9.954		423.315	19.442	19.406						
446.354	10.612			10.633		448.267	20.920	20.909						
448.825	10.678			10.699		473.440	22.371	22.423						
III	79.756			353.330	11.843	11.936	.04372	34.088		373.593	22.806	23.182	.09942	
				373.000	12.742	12.796		398.183		25.105	25.627			
				373.010	12.741	12.797		423.286		28.210	28.123			
				398.240	13.874	13.899		448.371		30.612	30.617			
				422.049	14.916	14.940		473.272		33.020	33.092			
		447.561	15.999	16.055	58.280	373.179		14.985	15.001	0.05615				
		476.731	17.330	17.331		398.327		16.397	16.347					
		498.288	18.321	18.273		90.253		348.202	9.310	9.307	.03281			
		35.796	398.426	24.605		24.698		373.763	10.200	10.145				
		421.337	26.873	26.850		398.072		11.015	10.943					
		IV(a)	89.812	442.649	28.723	28.851		.09391	58.280	373.179	14.985	15.001	0.05615	
				476.655	31.944	32.045			398.327	16.397	16.347			
				348.618	10.348	10.416			423.099	11.837	11.764			
				373.564	11.353	11.355			448.243	12.693	12.589			
				398.450	12.308	12.291			473.224	13.404	13.409			
423.734	13.260			13.243	58.514	348.167	13.464		13.616	.05329				
449.059	14.195			14.195		373.742	14.970		14.978					
473.462	15.090			15.113		398.078	16.305		16.276					
51.753	373.551			16.518		16.636	423.147		17.636	17.611				
398.384	18.193			18.159		448.218	18.938		18.947					
IV(b)	89.812			423.755	19.651	19.714	.06131		30.002	373.557	25.259	25.314	.11537	
				448.960	21.249	21.259			398.059	28.336	28.141			
				473.506	22.591	22.764			423.066	31.147	31.026			
				26.583	398.210	30.897			30.539	34.112	33.933			
				423.662	34.376	33.919			473.002	36.834	36.787			
		449.345	37.314	37.329	52.588	V		373.434	16.308	16.404	.06019			
		373.096	10.234	10.165		398.191		17.911	17.894					
		69.726	353.330	11.843		11.936		423.315	19.442	19.406				
			373.000	12.742		12.796		448.267	20.920	20.909				
			373.010	12.741		12.797		473.440	22.371	22.423				
			398.240	13.874	13.899	34.088		373.593	22.806	23.182	.09942			
			422.049	14.916	14.940	398.183		25.105	25.627					

where  $\log_{10} \delta = 1.0548 - 6.120/v$ . The units here are atmospheres, cc. per gram, and

$$T = 273.16 + t$$

$$R = 2.6421 \text{ cc.-atm.}$$

A comparison of the pressures calculated by this equation with the observed pressures is given in the table.

Summary

1. The pressure-volume-temperature relations for gaseous monomethylamine have been measured over a temperature range of 60 to 225°, a specific volume range of approximately 27 to 107 cc. per gram, and a pressure range of approximately 7.5 to 38 atmospheres.

2. An equation of the Keyes type has been fitted to these data; this equation is

$$p = \frac{RT}{(v - \delta)} - \frac{17,940}{(v + 1.759)^2}$$

where  $\log_{10} \delta = 1.0548 - 6.120/v$ . This equation reproduces the observed pressures satisfactorily.