η = viscosity in poises
σ = zero energy collision diameter in (Å) (a Lennard-Jones force parameter)
$\Phi(r)$ = intermolecular potential energy function
Ω = appropriate value of the collision integral (a function of kT/ϵ)

Subscripts

A, B, AB = molecular pairs (AA), (BB), and (AB), or (BA), respectively
i = ith component or species
mix = gaseous mixture
1, 2, 3 = numbers associated with the molecular pairs (AA), (BB), and (AB), or (BA), respectively

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Compressibility of Ammonia and its Mixtures with Nitrogen and Hydrogen

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OBJECTIVES AND SCOPE

The original objective of this work was to obtain compressibility data on the ternary system hydrogen-nitrogen-ammonia in order to permit calculations to be made of the effect of pressure on the equilibrium of the ammonia-synthesis reaction. For reasons which will be discussed presently the original objective was abandoned and the new one became the determination of the compressibility of pure ammonia and its mixtures with nitrogen at elevated pressures and temperatures.

An apparatus has been developed to take compressibility data from 500 to 2,500 atm. at temperatures ranging from 300° to 500°C. Compressibility data are presented for pure ammonia and a mixture of 19 mole % nitrogen and 81% ammonia at 350°, 400°, and 450°C. over the pressure range of 500 to 2,500 atm. Also data for pure ammonia at 300°C. and 500 to 1,500 atm. and a few points for the 37% nitrogen mixture at 350°C. are given.

REVIEW OF PREVIOUS WORK

Although a great many investigators have conducted compressibility studies on nitrogen and ammonia, very little work has been done above 300°C. and 1,000 atm. This review is confined to work either at 300°C. and above or at pressures greater than 1,000 atm. While Michels and co-workers (*23, 24*) provide the most accurate data on nitrogen to a pressure of 6,000 atm., the temperature range extends only to 150°C. Bartlett and co-workers (*1, 2*) conducted experiments to 400°C. but limited the pressures to 1,000 atm. Benedict (*4*) conducted a very thorough study of nitrogen at 5,800 atm., but the top temperature was 200°C. Recently Saurel and co-workers (*27*) have extended the ranges of temperature and pressure for this gas to 1,000°C. and 1,000 atm.

Ammonia has not been studied as extensively as nitrogen. Meyers and Jessup (*20*) did some early work to 300°C. and 28 atm. Beattie and Lawrence (*3*) obtained data at temperatures as high as 325°C. but limited the pressure to 130 atm.

More recent work was done by two investigators in Russia. Kazarnovskii (*15, 16*) has done considerable work on the ammonia, nitrogen, hydrogen system, and he also studied pure ammonia from 150° to 300°C. and 100 to 1,600 atm. This present study presents data that can be compared with the work of Kazarnovskii on ammonia at 300°C. and from 500 to 1,600 atm. Tsiklis (*28*) investigated ammonia compressibility at 150°C. and pressures in the range of 1,000 to 10,000 atm.

In contrast to the considerable amount of work that has been performed on the pure gases relatively little has been accomplished with mixtures of the two. Only one

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investigator has measured compressibilities of mixtures of nitrogen and ammonia. Kazarnovskii and co-workers (*16*) made measurements with a mixture of 55.60 mole % nitrogen and 44.40% ammonia from 150° to 300°C. and 100 to 1,600 atm.

For a more detailed review of the work in this field the reader is referred to Comings (*8*), where a complete literature survey of the P-V-T data for these gases as well as many others up to the year 1955 is presented.

EXPERIMENTAL METHODS

Apparatus for Ternary System

An apparatus was originally designed for use with the ternary system nitrogen-hydrogen-ammonia but was never successfully operated. Problems posed by the diffusion of hydrogen through metals and embrittlement caused by hydrogen led to a double-vessel design. This consisted of an inner thin-walled vessel which was the measuring pipet surrounded by a heavy-walled vessel to withstand the full pressure. By means of a special diaphragm indicator the pressure differential between the two vessels was to be monitored and controlled. Because of many difficulties with leaking seals, carry-over of oil vapor into the measuring vessel, and finally mechanical failure of the outer vessel this apparatus was abandoned in favor of a simpler design. This was made possible by the decision to limit the scope of the work to the binary system nitrogen-ammonia.

Choice of Method

There are three major static methods for determining compressibility data: the constant-volume method as developed by Bartlett and co-workers (*1, 2*), the variable-volume one perfected to such a high degree by Michels and Gibson (*25*), and the somewhat newer method developed by Burnett (*7*) and referred to by his name. The constant-volume method was chosen for this work.

In this method the gases are placed in a high-pressure vessel of calibrated volume that is immersed in a controlled-temperature bath. When temperature equilibrium is achieved, the pressure is measured with a dead-weight piston gauge. Following this the mass is determined by expanding to a low-pressure glass system of known volume.

The decision to use the constant-volume method was based on the relative simplicity of the construction and operation of the equipment and the ease of handling the data. Unlike the variable-volume method there is no loading problem, as the mass is determined by an expansion after the pressure measurement. In addition no delicate instrumentation is necessary to locate a mercury interface, as there is no need for a confining fluid.

Since no confining fluid is needed, the error introduced by contamination of the experimental system with vapor of this fluid is avoided. The usual fluid is mercury which has a vapor pressure of about 4.2 atm. at 450°C., and this would be increased somewhat by the high total pressure and the solvent effect of the gas. At one time the use of gallium was considered, but it was ruled out because of its rarity and cost.

Another advantage of this method is that the calculations are straightforward in contrast to the curve fitting and extrapolating to zero pressure necessary in the Burnett method.

A schematic diagram of the apparatus assembly is given in Figure 1.

Special Problems Posed by Ammonia

The use of ammonia, a condensible gas at the pressures involved in these experiments, posed some special problems. The critical temperature of ammonia is approximately 132°C. It was necessary therefore to heat all the parts of the equipment located outside of the high-temperature bath that were exposed to the ammonia to a temperature above this, say to 150°C. This is necessary to prevent either the condensation of the pure ammonia or a phase separation when the nitrogen was present. The 150°C. limit was dictated by some of the materials of construction.

There was also a question of the decomposition of the ammonia at the temperatures to be used for the compressibility measurements. Although the rate of decomposition would normally be low at these temperatures, the iron surface might act as a catalyst and cause significant reaction. If appreciable decomposition did occur, it should be evident from an increase in pressure, and no such increase was observed even when ammonia at 300°C. and 1,000 atm. was allowed to remain in the vessel for 24 hr.

As a further test samples of the ammonia were periodically run through a chromatograph to test for the presence of impurities. Hydrogen was never detected in any of these samples.

Keyes (*17*) indicated that a trend exhibited by some of his data could be explained by adsorption of the ammonia on the walls of his vessels. He stated that this problem could be overcome by the use of a steel vessel with polished walls.

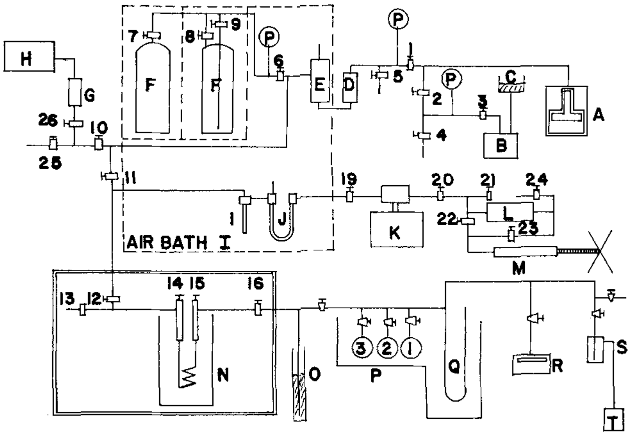

Fig. 1. Schematic diagram of the apparatus: A. High pressure intensifier, B. continuous 15,000 lb./sq.in.abs. oil pump, C. oil reservoir, D. oil leg of liquid piston pump, E. gas leg of liquid piston pump, F. gas storage vessels, G. filters, H. Norwalk compressor, I. mercury trap, J. mercury U tube, K. dead-weight piston gauge, L. intensifier, M. oil injector, N. pipet and salt bath assembly, O. Safety tube, P. expansion bulbs and water bath, Q. mercury manometer, R. vacuum gauge, S. vacuum trap, T. vacuum pumps, 1, 2, 3. expansion vessels, 4-26 inc. denote valves.

Adsorption of ammonia in the pressure pipet would have the effect of increasing the mass at each pressure level. This would tend to decrease the value of the compressibility factor. As the compressibility factors in the present work are higher than the comparable values reported by Kazarnovskii, it is believed that adsorption in the pipet is not significant.

Adsorption on the walls of the glass system however was another question. Adsorption in this area would tend to reduce the calculated mass, thus increasing the compressibility factor. Some calculations were performed with the experimental adsorption data of Crespi and co-workers (*9, 10*). These calculations indicated that the maximum effect would be 0.01 to 0.02% of the total mass involved.

This is well within the experimental error of the present work.

The production of known mixtures of nitrogen and ammonia of uniform composition also involved some difficult problems not encountered with the type of mixtures most commonly studied in previous work on compressibility. This stemmed both from the fact that ammonia is a liquid at room temperature and elevated pressure, and from the very slow rate of mixing of very dense gases in the absence of mechanical agitation.

Description of the Apparatus

Pressure Generating System The pressure-generation system consists of a continuous 15,000 lb./sq.in.abs. oil pump, a one-stroke intensifier good to 60,000 lb./sq.in. abs., and a liquid-piston pump. The oil pump is used both to provide the initial pressure of 15,000 lb./sq.in.abs. whenever necessary and to return the intensifier piston to its starting position when it had reached the end of its stroke. The intensifier was used to raise the pressure from 15,000 lb./sq.in.abs. to the desired conditions. The transmitting fluid used for both pieces of equipment was 90% kerosene and 10% heavy medium oil. The oil was added to give better lubricating properties to the fluid.

The primary function of the liquid-piston pump is to provide a mercury interface between the gas and the oil from the intensifiers for the purpose of preventing contamination of the gas with oil. In some of the early runs, when the oil leg of this pump was kept in an air bath at 150°C., oil did succeed in bypassing the mercury in some unexplained way, but subsequent steps that were taken (mainly placing this leg at room temperature) reduced this to an insignificant amount. The pump consists of two steel vessels connected in a U with an electric contact on the mercury side to indicate the level.

Pressure Measurement Spring gauges were used for pressure measurement during the startup period of a run, but all final recorded measurements were made with a dead-weight piston gauge. The one used in this work was the one used by Bennett (*5*) and was modeled after the design of Keyes (*18*). There were several pistons, but only the 3/32-in. piston was used for the entire range of this work. The mercury-filled U tube associated with the dead-weight piston gauge is made of 9/16-in. high-pressure tubing bent into shape, with an electrode in the closure on the gas side. The merucry in this unit serves two functions; it separates the oil from the gas, and it provides a convenient method of determining the balance point on the dead-weight piston gauge.

When the weight is slightly too high on the piston gauge, the mercury contacts the electrode activating a light. When the extra weights are removed, the light goes out. This is also one means of determining the sensitivity of the piston gauge at each pressure measurement.

High-Pressure Pipet This is the vessel in which the sample of gas whose compressibility is to be determined is isolated at a given pressure and temperature. It consisted of a coil of ¼ by 1/16 in., chrome-molybdenum steel tubing rated for 100,000 lb./sq.in. The calibrated volume of this vessel included the volume of the coil itself, as well as the volume of the removable seats on the inlet and outlet valves. These were special valves designed for high temperature, 60,000 lb./sq.in.abs. service. The special feature of these valves was the long stem that permitted the packing to be placed above the level of the salt in the controlled temperature bath. The entire valve seat as well as the tip of the stem however was fully immersed.

A radiation shield was located between the packing level and the salt level. At the same time cooling coils were placed just above the radiation shield to prevent the temperature of the packing from exceeding 200°C. The original packing consisted of neoprene O rings with leather back-up washers. When these failed owing to the high-temperature service, they were replaced with glass-impregnated teflon, which proved to be quite satisfactory.

The entire assembly was seasoned by subjecting it to 450°C. and 52,000 lb./sq.in.abs. before any runs were made.

Temperature Measurement and Control The constant-temperature bath was a mechanically stirred salt bath with a commercially available mixture of nitrates and heated by two 2,200-w. immersion heaters. The electric motor was mounted in such a way that it was protected from overheating by the bath, and the upper bearing of the impellor was protected from overheating by a radiation fin. The bottom bearing was in the salt bath and being lubricated only by the molten salt the wear was rapid and this bearing had to be replaced about every 2 or 3 mo.

To control the bath temperature within 0.1°C. a relatively inexpensive homemade design proved to be quite satisfactory. The sensing element used at first consisted of two iron-constantan thermocouples in series. The difference between the electromotive force of the couples and a reference voltage derived from a potentiometer was amplified about five times and used to operate a relay circuit composed of two Sensitrol relays which controlled the current to the heaters. This system was reliable and controlled the temperature to 0.025°C. The need to maintain the reference thermocouple junction at 0°C. for long periods of time posed a problem which was finally solved by using as the sensing element the platinum resistance thermometer already in use for temperature measurement. The very small current flow through the platinum had a negligible effect on the temperature measurement.

Mass Measurement The mass-measuring system consists of three large 2-liter glass bulbs connected to a mercury manometer and an evacuation system. The entire glass system is immersed in a constant-temperature water bath contained in a wooden vessel lined with copper. Agitation is provided by two stirrers driven by a small motor. The temperature was controlled to 0.01°C. at a temperature of 25°C. by a mercury sensing element in conjunction with a thyratron relay. The temperature of the bath was measured with a Beckman thermometer. The pressure of the expanded gas was determined from the height of the mercury in the manometer as read with a cathetometer. Knowing the pressure, temperature, and volume of the gas expanded into this system, one can calculate its mass from the known behavior of the gas at low pressure.

Miscellaneous The high-pressure tubing and the valves were rated for 60,000 lb./sq.in.abs. service at room temperature. Both the tubing and the valves are standard equipment readily available commercially. All of the high-pressure connections are standard ¼-in. cone joints (*13*) unless otherwise specified.

The gas-storage system as well as the gas leg of the liquid-piston pump and the U tube of the piston gauge were all heated to 150°C. by air baths constructed of angle-iron frames with walls of transite and asbestos. The heat was supplied by finned strip heaters. Strip heaters were also located at the base of the storage cylinders to provide a gradient of 40° to 50°C. to induce convection currents that would aid mixing of the gases.

All the valves and tubing that came in contact with the gases were also heated electrically to 150°C. by resistance ribbon wound around the tubing and valves. Asbestos tape provided the necessary insulation. The temperature profile in the air baths as well as along the tubing and the valves were measured with iron-constantan thermocouples.

Calibrations

The 3/32-in. piston of the dead-weight piston gauge was calibrated by comparison with a 3/16-in. piston which in turn was calibrated against the vapor pressure of carbon dioxide at 0°C. (2613.88 mm. of Hg.). This is an average of the values of Bridgeman (*6*), Roebuck and Cram (*26*), and Meyers and Van Dusen (*21*). Suitable small corrections were made for distortions of the gauge due to pressure and temperature.

The volume of the 2-liter glass containers for mass determination was measured by weighing with and without a water filling and that of the connecting tubing by filling with gas from a known volume.

The high-pressure pipet was calibrated by expanding compressed nitrogen from it into the low-pressure measuring system. From the known compressibility data for nitrogen at the pressure and temperature of the calibrations the volume could be calculated. The calibration was performed at 300°C. and 438.83 atm., and the compressibility data of Bartlett and co-workers (*1*) as smoothed and tabulated by Deming and Shupe (*11*) were used to obtain the value $Z = 1.2381$. The excellent and probably more accurate data of Michels and co-workers (*23, 24*) could not be used because they extend only to 150°C. To correct the volume from the calibration conditions to those of an experiment use was made of the known value of thermal expansion coefficient and Love's equation (*19*) for the pressure effect.

Preparation and Analysis of the Gas Mixtures

The ammonia and nitrogen were stated by the suppliers to have purities of 99.99%. Ammonia was transferred as liquid from a commercial cylinder to the storage vessels by maintaining a temperature difference, the amount transferred being determined by weighing. Mixtures were prepared by adding nitrogen from a storage system at 15,000 lb./sq.in.abs. to ammonia stored at approximately 150°C. to keep it in the gaseous state. Analysis of a mixture was performed volumetrically in a modified Burrell apparatus by absorption of ammonia in an acid solution. Erratic results were at first obtained in the analysis of the gases which were eventually traced to a faulty sampling technique. Sampling was accomplished by expanding the gas from the storage vessel to the gas leg of the liquid-piston pump. When the valve was first cracked to do this, there was an initial pressure drop of 6,000 lb./sq.in.abs. If this valve were opened too rapidly, the sudden expansion of the gas cooled it sufficiently to result in condensation of some of the ammonia. This probably accounted for the erratic results obtained in the analysis at the start of the work. Once this was realized, it was corrected by a very careful handling of the valves, and thereafter the analysis yielded results that were reproducible to 0.1%.

During the course of the analysis it became apparent from the slow drift in composition of successive samples that the mixing of the gases was exceedingly slow. Wiebe and Gaddy (*29*) have also pointed this out. In the present work, even with a temperature gradient of 50°C., induced just to help mixing, it took two weeks to mix. Samples were taken from the top and the bottom of one of the storage vessels and compared. In the other vessel they were taken only at the top and compared with the previous day's results.

Recirculation of the gases by the use of a pump was contemplated as a means of mixing, but no facilities were available that could pump hot gases without contaminating them.

Further details on the apparatus and the operating procedure may be obtained by consulting the dissertation of the junior author, I. M. Lichtblau.

RESULTS

Tables 1 and 2 contain data that are smoothed and interpolated to even intervals of pressure and temperature. The compressibility factors are tabulated for the pressure at each temperature and composition investigated. The smoothing and interpolation were performed on an IBM-709 digital computer with an equation of the following form:

$$P = a_1 d + a_2 d^2 + \dots + a_n d^n + a_0 dP$$

The compressibility factors were then calculated from the pressures and densities at each temperature.

TABLE 1. SMOOTHED COMPRESSIBILITY DATA

(*A*) Pure Ammonia

300°C.		350°C.	
P(atm.)	Z	*P*(atm.)	Z
506.2	0.7346	517.3	0.8239
760.7	0.8214	775.1	0.8868
1054.1	0.9623	1013.5	0.9768
1502.0	1.1997	1497.7	1.2012
		1989.3	1.4399
		2215.1	1.5505
		2418.2	1.6480

400°C.		450°C.	
P(atm.)	Z	*P*(atm.)	Z
513.9	0.8875	520.3	0.9388
780.2	0.9463	766.0	0.9740
1026.8	1.0199	1022.5	1.0425
1262.8	1.1071	1269.7	1.1262
1495.8	1.2022	1555.5	1.2318
2064.1	1.4573	1797.0	1.3277
2228.8	1.5267	2015.1	1.4121
2366.6	1.5869	2280.0	1.5151

(*B*) 81.0% Ammonia 19.0% Nitrogen

350°C.		400°C.		450°C.	
P(atm.)	Z	*P*(atm.)	Z	*P*(atm.)	Z
503.8	0.9509	518.5	0.9957	511.6	1.0160
774.6	1.0242	753.6	1.0502	758.2	1.0760
1042.6	1.1369	1044.8	1.1583	1036.2	1.1632
1553.9	1.3769	1260.5	1.2345	1296.3	1.2564
2027.7	1.5974	1548.4	1.3634	1543.0	1.3524
2534.7	1.8360	2006.0	1.5616	2053.4	1.5449
		2529.2	1.7825	2505.4	1.7198

DISCUSSION OF RESULTS

Error Analysis

The precision of the data is an indication of the reproducibility, or the randomness of the errors in making a series of measurements. It was estimated from the fit of the data to the polynomial equation that the precision of the data was better than 0.10% for most of the isotherms.

The absolute error is an indication of the nearness of the data to the true value. This error can be calculated by summing both the random errors and the systematic errors. The former arise from all the direct measurements of pressure and temperature, while the latter arise from the uncertainty of the calibrations, as well as the uncertainty in the corrections for the effect of temperature and pressure on both the dead-weight piston-gauge constant and the volume of the high-pressure pipet. The sum of these potential errors indicated that the maximum absolute error is approximately 0.32%.

Comparison with Literature Data

As was mentioned before very few data exist in the literature at the temperatures of this study. There is however a slight overlap with data of Kazarnovskii on pure ammonia. A comparison of his data at 300°C. between 500 and 1,500 atm. with the data of this study shows that the data in the latter are 1.4% higher than the data of Kazarnovskii. This apparent discrepancy would arise if the gas contained some impurities, adsorption on the glass in the low-pressure system took place, there was catalytic decomposition, or the calibration of the high-pressure pipet gave too large a volume.

An analysis of the gas showed that within the precision of the gas chromatograph used there were no impurities present. Calculations based on the data of Crespi and co-workers (*9*, *10*) indicated that the adsorption of ammonia on the glass system at atmospheric pressure would be negligible. The fact that hydrogen did not show up in the gas analysis indicated that there was no decomposition of the ammonia. The reproducibility of the calibration of the pipet provides some justification for assuming the calibration to be correct. Adsorption in the high-pressure vessel could not contribute to the discrepancy, as this would tend to lower the compressibility factor rather than raise it.

TABLE 2. INTERPOLATED COMPRESSIBILITY DATA

(*A*) Pure Ammonia

P(atm.)	300°C.	350°C.	400°C.	450°C.
500	0.7338*	0.8207*	0.8846*	0.9374*
750	0.8166	0.8790	0.9386	0.9707
1,000	0.9353	0.9711	1.0109	1.0355
1,250	1.0627	1.0829	1.1020	1.1192
1,500	1.1986	1.2023	1.2040	1.2112
1,750	—	—	—	1.3099
2,000	—	1.4468	1.4300	1.4062
2,250	—	1.5673	1.5359	1.5035
2,500	—	1.6871*	1.6453*	1.6002*

(*B*) 81.0% Ammonia 19.0% Nitrogen

P(atm.)	350°C.	400°C.	450°C.
500	0.9505*	0.9933*	1.0137*
750	1.0152	1.0491	1.0737
1,000	1.1178	1.1395	1.1509
1,250	1.2339	1.2292	1.2392
1,500	1.3513	1.3423	1.3347
2,000	1.5850	1.5590	1.5241
2,500	1.8209	1.7704	1.7177

* Extrapolated.

There is a question however as to the suitability of the variable-volume method used by Kazarnovskii for compressibility determinations above 150°C. In the first place the mercury confining fluid at these temperatures would provide an uncertain curvature at the interface. In the second place the correction for the presence of mercury in the gas phase may be considerable at the high densities involved. No information is available on how Kazarnovskii made the correction, but if he merely considered the effect of the hydrostatic pressure on the vapor pressure (so-called *Poynting effect*) as is commonly done, the correction will be much too small and even of the wrong sign as pointed out by Jepson and Rowlinson (*14*). The correction would increase the observed pressure, and this is in the right direction to account for the difference between the two sets of results. Keyes (*17*) suggested that a vessel constructed of glass, as is the case of the pipet in Kazarnovskii's work, could provide a suitable surface for adsorption of ammonia at high pressure. Michels et al. (*22*) indicated that ammonia will combine with mercury to form unstable compounds at high pressure. It is possible that any one of these considerations could have caused an error in the compressibility data.

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