Phase Behavior in the Hydrogen-Ammonia System

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The volumetric and phase behavior of ammonia has been investigated in some detail (*4–6*), and the results are available to the engineering profession in a tabular form (*3*) utilized primarily by the refrigeration industry. These data supply the specific volume, enthalpy, and entropy of the liquid and gas phases of ammonia as a function of pressure and temperature. Detailed information concerning the vapor pressure of ammonia is available also (*6*). The volumetric behavior of hydrogen has been studied over the temperature range 40° to 250° F. (*7,13*). In addition, the volumetric behavior of mixtures of hydrogen and ammonia has been investigated (*14*).

The composition of the bubble point liquid of the hydrogen-ammonia system has been determined as a function of pressure and temperature with sufficient detail and accuracy (*14*) to make unnecessary further studies of this composition. However, satisfactory measurements of the composition of the gas phase of heterogeneous mixtures of hydrogen and ammonia have not come to the authors' attention. As part of a more general study of the transport properties of ammonia in the ammonia-hydrogen-nitrogen system, a study of the composition of the gas phase of heterogeneous mixtures of hydrogen and ammonia was made at temperatures between 40° and 250° F. and at pressures as high as 6000 p.s.i.

In the present investigation the data of Wiebe and Gaddy (*13*) on the volumetric behavior of hydrogen were used. The volumetric measurements of Cragoe and others (*4–6*) were employed to establish the specific volume of ammonia, and the data of Wiebe and Tremearne (*14*) were used to establish the volumetric behavior of the liquid phase of mixtures of hydrogen and ammonia in heterogeneous equilibrium.

EQUIPMENT AND METHODS

A detailed description of the apparatus used for this investigation is available (*12*). The apparatus consisted, in principle, of a stainless-steel vessel in which heterogeneous mixtures of hydrogen and ammonia were confined over mercury. The pressure vessel was provided with a mechanical agitator driven through a stainless-steel wall by a rotating electromagnet. The pressure vessel was placed within an agitated oil bath, the temperature of which was controlled within small limits by a suitable electronic modulating circuit (*10*). Provision was made for the introduction and withdrawal of known amounts of mercury, thus permitting the total volume of the pressure vessel, exclusive of the space filled with mercury, to be determined with an uncertainty of the order of 0.25%. The volumetric measurements made in this way are of no direct consequence in the current investigation.

The pressure was measured with a balance (*12*) which was calibrated against the vapor pressure of carbon dioxide (*2*). The pressure within the equilibrium vessel was known within 0.03% or 0.2 p.s.i., whichever was the larger measure of uncertainty. The temperatures were determined with a platinum resistance thermometer of the strain-free type (*8*). This thermometer was compared with a similar instrument which had been recently calibrated by the National Bureau of Standards. Experience indicates that the temperature of the heterogeneous mixture of hydrogen and ammonia was known within 0.02° F. of the international platinum scale (*1*).

The sample of the gas phase was withdrawn from the pressure vessel through an appropriate connection after the attainment of equilibrium. The withdrawal process was carried out under isobaric-isothermal conditions. Mercury was introduced at a rate sufficient to keep the pressure within the equilibrium vessel constant. The composition of the gas withdrawn was determined by two different methods. In one instance, the gas was passed through a condenser (*9*) which was maintained at the pressure and temperature of liquid air, and the quantity of ammonia collected was determined by gravimetric methods. The quantity of hydrogen removed was determined by the change in pressure in an evacuated glass bulb kept at a constant temperature. The second method of analysis involved the direct measurement of the specific weight of the gas phase withdrawn. From a knowledge of the volumetric behavior of gaseous mixtures of hydrogen and ammonia (*14*), it was a simple matter to evaluate the composition of the phase. These two methods gave satisfactory agreement, and it is believed that the composition of the gas phase withdrawn from the equilibrium vessel was known within 0.002 mole fraction of ammonia. At each equilibrium state two samples of the gas phase were withdrawn, thus affording a check upon the duplicability of the withdrawal process.

MATERIALS

The hydrogen used in this investigation was obtained from commercial sources and was prepared by electrolytic means. The hydrogen was passed over anhydrous calcium sulfate and then through a condenser which was maintained at the temperature of liquid nitrogen. Spectroscopic analyses of the hydrogen indicated it contained less than 0.003 mole fraction of impurities after this treatment. The ammonia was purchased as the anhydrous material and was dried by contact with anhydrous calcium sulfate. It was found that the vapor pressure of the ammonia varied with quality less than 0.02 p.s.i. at a constant temperature of 100° F. On the basis of these findings it was estimated that the ammonia contained less than 0.002 mole fraction of impurities.

EXPERIMENTAL RESULTS

Table I records the composition of the gas phase withdrawn from heterogeneous mixtures of hydrogen and ammonia. The experimental data for the gas phase for each of the five temperatures involved in this study are depicted in Figure 1 on a pressure-composition diagram. The standard error of estimate from the smooth curves representing compositions of the dew point gas as a function of pressure and temperature was 0.0013 mole fraction of hydrogen. This standard error of estimate was

Table I. Experimental Measurements in Gas Phase of Hydrogen-Ammonia System

Pressure, P.S.I.	Compn., Mole Fraction Hydrogen	Pressure, P.S.I.	Compn., Mole Fraction Hydrogen
40° F.		220° F.	
223.17	0.6601	1556.16	0.2312
378.94	0.7907	1746.45	0.2772
499.16	0.8370	1967.84	0.3227
699.92	0.8804	2190.01	0.3567
1133.06	0.9218	2502.02	0.4066
1504.94	0.9401	2810.52	0.4418
2091.63	0.9540	3083.67	0.4706
3200.43	0.9638	3406.84	0.4970
4600.55	0.9702	3718.20	0.5166
5213.98	0.9707	4003.30	0.5311
		4497.34	0.5600
100° F.		4895.14	0.5743
		5539.21	0.5970
356.19	0.3743	6046.12	0.6093
523.42	0.5551		
760.64	0.6732	250° F.	
819.50	0.6956		
899.73	0.7279	2524.72	0.2367
1010.07	0.7439	3123.68	0.2884
1212.84	0.7878	4173.62	0.3430
1690.47	0.8363	4604.71	0.3534
2076.92	0.8588		
2600.99	0.8810		
3068.58	0.8912		
4443.12	0.9166		
5908.38	0.9262		
160° F.			
784.32	0.3044		
1056.95	0.4444		
1430.25	0.5620		
1810.86	0.6301		
2344.57	0.6912		
3400.04	0.7596		
4512.68	0.7986		
5499.56	0.8185		

determined on the assumption that all the error lay in the mole fraction of hydrogen and none in the establishment of the prevailing equilibrium pressure and temperature.

The experimental data of Wiebe and Tremearne (*14*), were used to establish the composition of bubble point liquid as a function of pressure and temperature. The standard error of

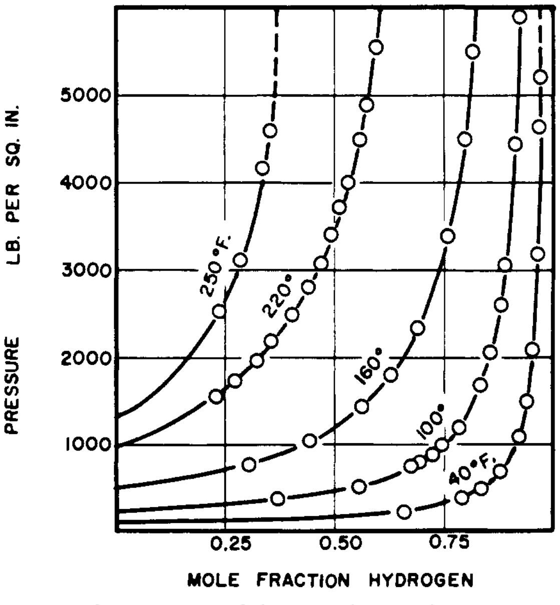

Figure 1. Composition of the gas phase in heterogeneous mixtures of hydrogen and ammonia

Table II. Composition of Coexisting Liquid and Gas Phases in Hydrogen-Ammonia System

Pressure, P.S.I.	Composition, Mole Fraction Hydrogen		Equilibrium Ratio	
	Dew point	Bubble point	Hydrogen	Ammonia
		40° F.		
73.3[a]	0	0	. . .	1.0000
500	0.8370	0.0021	398.6	0.1633
1000	0.9144	0.0040	228.6	0.0859
1500	0.9401	0.0055	170.9	0.0602
2000	0.9524	0.0070	136.0	0.0479
2500	0.9595	0.0085	112.9	0.0408
3000	0.9640	0.0102	94.51	0.0364
3500	0.9664	0.0120	80.53	0.0340
4000	0.9690	0.0140	69.21	0.0314
4500	0.9705	0.0160	60.66	0.0300
5000	0.9715	0.0181	53.67	0.0290
5500	0.9718	0.0203	47.87	0.0288
6000	0.9720	0.0225	43.20	0.0286
		100° F.		
211.9[a]	0	0	. . .	1.0000
500	0.5350	0.0025	214.0	0.4662
1000	0.7490	0.0056	133.8	0.2524
1500	0.8183	0.0085	96.27	0.1793
2000	0.8562	0.0115	74.45	0.1457
2500	0.8779	0.0147	59.72	0.1239
3000	0.8923	0.0181	49.30	0.1090
3500	0.9033	0.0217	41.63	0.0982
4000	0.9110	0.0255	35.68	0.0914
4500	0.9165	0.0295	31.07	0.0860
5000	0.9215	0.0335	27.48	0.0812
5500	0.9246	0.0375	24.66	0.0784
6000	0.9270	0.0413	22.45	0.0761
		160° F.		
492.8[a]	0	0	. . .	1.0000
500	0.0099	0.0001	99.00	0.9902
1000	0.4220	0.0065	64.92	0.5818
1500	0.5765	0.0115	50.13	0.4284
2000	0.6554	0.0170	38.55	0.3510
2500	0.7038	0.0230	30.60	0.3032
3000	0.7395	0.0290	25.50	0.2683
3500	0.7640	0.0350	21.83	0.2446
4000	0.7831	0.0410	19.10	0.2262
4500	0.7980	0.0470	16.98	0.2120
5000	0.8098	0.0530	15.28	0.2008
5500	0.8185	0.0590	13.87	0.1929
6000	0.8266	0.0650	12.72	0.1855
		220° F.		
989.5[a]	0	0	. . .	1.0000
1000	0.0086	0.0004	21.50	0.9918
1500	0.2162	0.0115	18.80	0.7930
2000	0.3300	0.0226	14.60	0.6855
2500	0.4056	0.0336	12.07	0.6151
3000	0.4620	0.0450	10.27	0.5634
3500	0.5024	0.0560	8.971	0.5271
4000	0.5343	0.0670	7.975	0.4991
4500	0.5580	0.0775	7.200	0.4791
5000	0.5788	0.0885	6.540	0.4621
5500	0.5952	0.0995	5.982	0.4495
6000	0.6096	0.1105	5.517	0.4390
		250° F.		
1347[a]	0	0	. . .	1.0000
1500	0.0530	0.0102	5.196	0.9568
2000	0.1593	0.0309	5.155	0.8675
2500	0.2332	0.0490	4.759	0.8063
3000	0.2795	0.0650	4.300	0.7706
3500	0.3128	0.0805	3.886	0.7474
4000	0.3360	0.0953	3.526	0.7339
4500	0.3528	0.1110	3.178	0.7300
5000	0.3615	0.1247	2.899	0.7295
5500	0.3679	0.1367	2.691	0.7322
6000	0.3701	0.1500	2.467	0.7411

[a] Vapor pressure of ammonia, p.s.i.

estimate of these experimental data from smooth curves of bubble point pressure as a function of composition and temperature was 0.0001 mole fraction of hydrogen.

Smoothed values of the mole fraction of hydrogen in the liquid and gas phases are presented in Table II together with the equilibrium ratio. The equilibrium ratio is defined by

$$K_k = \frac{y_k}{x_k} \tag{1}$$

where y_k represents the mole fraction of component k in the gas phase and x_k represents the mole fraction of component k in the liquid phase.

The product of the equilibrium ratio and the pressure, PK, which provides a convenient means of representing the phase behavior of such binary systems (*11*), is presented in Figure 2. In Figure 3 the data for ammonia are shown upon an enlarged scale for the region of low pressure. These data indicate that the critical pressure of this system is markedly in excess of 6000 p.s.i.

The present data serve to establish the phase behavior of the hydrogen-ammonia system at temperatures between 40° and 250° F. for pressures up to 6000 p.s.i. The results indicate that this system exhibits the phase behavior normally encountered in binary systems in which there is no chemical reaction between the components.

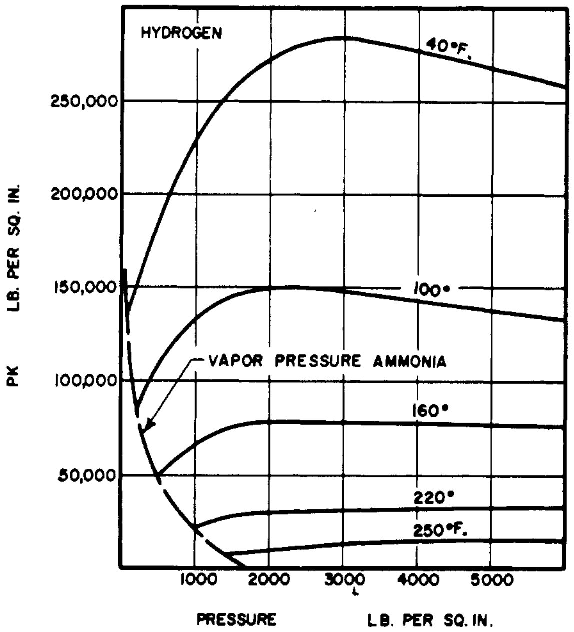

Figure 2. Equilibrium ratios for hydrogen in the hydrogen-ammonia system

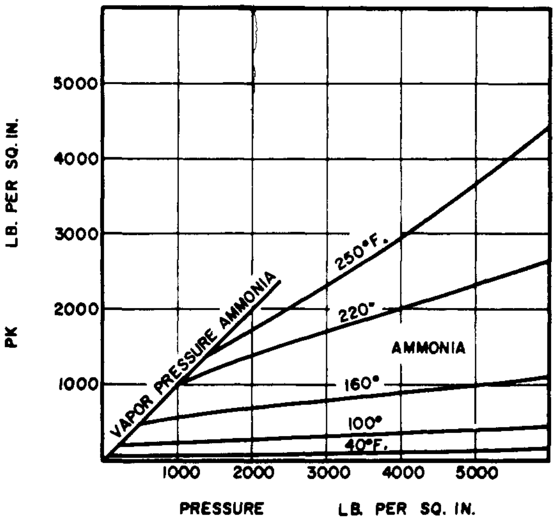

Figure 3. Equilibrium ratios for ammonia in the hydrogen-ammonia system

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