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Interim Report

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This report is to be superseded by a future publication which will receive general distribution and should be cited as a reference. Please consult the NBS Office of Technical Information and Publications to obtain the proper citation.

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The Equation of State for Ammonia*

by

Lester Haar and John Gallagher

1. Introduction

This report has been prepared in answer to several urgent requests for detailed computer programs for the thermodynamic properties of ammonia. In it we present a description of an extensive correlation of the thermodynamic properties of ammonia published elsewhere[1], along with basic equations for the description of the properties of ammonia and detailed listings of computer programs based on these equations. With this information, thermodynamic properties can be calculated for temperatures ranging from the triple point temperature to about 5/3 the critical temperature and for pressures ranging from the dilute gas to about 8000 bars. The reference state for all properties is the ideal gas at zero kelvin. The physical constants used are consistent with those recommended by Cohen and Taylor[2]. The mass of a mole of ammonia was taken to be 17.0306 grams[3].

2. The derivation of the thermodynamic surface.

In the correlation, selected P,ρ,T data were fitted to an analytic equation of state in the least squares sense. A detailed discussion of the process of data selection and of selection of parts of the analytic equation is contained in reference 1. The equation so obtained contains the pressure as a 44 term double power series function of temperature and density. The resulting equation can be used to

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reproduce all the available P,ρ,T experimental data as well as to produce limited extrapolations (based on thermodynamic arguments) of the surface into important regions where data are sparse. The range of the equation is bounded at low temperatures by the triple point temperature (195.48K) and the melting curve for the liquid, and at high temperatures by the isotherm at 750K (which is approximately 5/3 the critical temperature). The pressure range extends to 8,000 bar. No mathematical constraints were imposed on the equation, and only P,ρ,T data were used in the least squares fit with the sole exception that values of vapor pressure were explicitly employed in regard to satisfying conditions of phase equilibrium.

Following Keenan et al.[4] the Helmholtz free energy function was represented in reference 1 as the sum of two terms, the first being the contribution from the equation of state and the second a function of temperature only referring to the properties of the ideal gas. Thus the Helmholtz free energy was expressed

$$A(\rho,T) = \bar{A}(\rho,T) + A^{o}(T), \qquad (1)$$

where $A^{o}(T)$ is the contribution of the ideal gas. T is the absolute temperature in kelvins and ρ the density in grams per cm^3. A quantity $Q(\rho,T)$ was defined by

$$\bar{A}(\rho,T) \equiv RT\,[\ln \rho + \rho Q\,(\rho,T)] \qquad (2)$$

Since $\quad P = \rho^2\, \partial A/d\rho,$

Eqs. (1) and (2) yield

$$P = \rho RT\,[1 + \rho Q + \rho^2\, \partial Q/\partial\rho]. \qquad (3)$$

Note that

$$Q\ (\rho=0) = B_2, \tag{3a}$$

where B_2 is the second virial coefficient. The form chosen for Q was

$$Q = \sum_{i=1}^{9} \sum_{j=1}^{6} a_{ij}\, \rho^{i-1} (\tau-\tau_c)^{j-1}, \tag{4}$$

where $\tau = \frac{500}{T}$, $\tau_c = 1.2333498$ and R is the gas constant. Eq. (3) for the pressure was fitted in the least squares sense to the experimental P,ρ,T data. The results of this fit are values for the constants a_{ij} listed in table 1. ($a_{ij} = 0$ for all i,j pairs not listed in table 1). By differentiation of eq (1), the various thermodynamic quantities can be expressed in terms of Q:

the entropy,

$$S(\rho,T) = R[\ell n\ \rho + \rho Q - \rho\tau\ \partial Q/\partial\tau] + S^o(T), \tag{5}$$

the internal energy,

$$E(\rho,T) = R\rho T\tau\partial Q/\partial\tau + E^o(T), \tag{6}$$

the constant volume heat capacity,

$$C_v(\rho,T) = -\ R\rho\tau^2\ \partial^2 Q/\partial\tau^2 + C_v{}^o, \tag{7}$$

Table 1

i	j	A_{ij}
1	1	-6.453022304053
1	2	-13.719926770503
1	3	-8.100620315713
1	4	-4.880096421085
1	5	-12.028775626818
1	6	6.806345929616
2	1	8.080094367688
2	2	14.356920005615
2	3	-45.052976699428
2	4	-166.188998570498
2	5	37.908950229818
2	6	-40.730208333732
3	1	1.032994880724
3	2	55.843955809332
3	3	492.016650817652
3	4	1737.835999472605
3	5	-30.874915263766
3	6	71.483530416272
4	1	-8.948264632008
4	2	-169.777744139056
4	3	-1236.532371671939
4	4	-7812.161168316763
4	5	1.779548269140
4	6	-38.974610958503
5	1	-66.922858820152
5	2	-1.753943775320
5	3	208.553371335493
5	4	21348.946614397509
6	1	247.341745995422
6	2	299.983915547501
6	3	4509.080578789798
6	4	-37980.849881791548
7	1	-306.557885430971
7	2	24.116551098552
7	3	-9323.356799989199
7	4	42724.098530588371
8	1	161.791003337459
8	2	-507.478070464266
8	3	8139.470397409345
8	4	-27458.710626558130
9	1	-27.821688793683
9	2	298.812917313344
9	3	-2772.597352058112
9	4	7668.928677924520

the enthalpy function,

$$H(\rho,T) = RT[\rho Q + \rho^2\ \partial Q/\partial\rho + \rho\tau\ \partial Q/\partial\tau + 1] + E^o\ (T), \qquad (8)$$

the constant pressure heat capacity,

$$C_p\ (\rho,T) = C_v + R\cdot\frac{\alpha}{\beta}\ , \qquad (8a)$$

where,

$$\alpha = 1 + \rho Q + \rho^2\ \partial Q/\partial\rho - \rho\tau\ \partial Q/\partial\tau - \rho^2\tau\ \partial^2 Q/\partial\tau\partial\rho\ ,$$

and

$$\beta = 1 + 2\ \rho Q + 4\ \rho^2\ \partial Q/\partial\rho + \rho\partial^2 Q/\partial\rho^2,$$

the heat capacity for the saturated fluid,

$$C_S = C_P - \frac{T}{\rho^2}\ \frac{(\partial P/\partial T)_\rho}{(\partial P/\partial\rho)_T}\cdot\frac{dP_S}{dT}\ , \qquad (9)$$

where P_S is the vapor pressure of the liquid.

S^o, E^o and $C_v{}^o$ are the corresponding contributions obtained from $A^o(T)$:

$$A^o(T) = (G^o - E^o_o) - RT(1 + \ln 4.8180\ T)\ ,$$

$$S^o = -\frac{d}{dT}A^o(T),$$

$$E^o = A^o(T) - T\frac{dA^o(T)}{dT}, \qquad (10)$$

$$C_v{}^o = -T\ d^2\ A^o(T)/dT^2,$$

where G^o is an analytic representation of the results reported by Haar[5] for the properties of the ideal gas state,

$$\frac{G^o - E^o_o}{RT} = a_1 \ell n\, T + \sum_{i=2}^{11} a_i T^{i-3}, \qquad (10a)$$

where E^o_o is the energy for the ideal gas at 0 K. The coefficients a_i are listed in table 2.

Table 2

$a_1 = -3.872727$

$a_2 = .64463724$

$a_3 = 3.2238759$

$a_4 = -.0021376925$

$a_5 = .86890833 \mathrm{x} 10^{-5}$

$a_6 = -.24085149 \mathrm{x} 10^{-7}$

$a_7 = .36893175 \mathrm{x} 10^{-10}$

$a_8 = -.35034664 \mathrm{x} 10^{-13}$

$a_9 = .2056303 \mathrm{x} 10^{-16}$

$a_{10} = -.6853420 \mathrm{x} 10^{-20}$

$a_{11} = .9939243 \mathrm{x} 10^{-24}$

The heat capacity values and the other thermodynamic functions calculated from Eq.(10a) for the temperature range $100 \text{ K} \leq T \leq 1000 \text{ K}$ agree with those tabulated in reference 5 to within the accuracy of those values.

Though Eqs. (1-10a) are complete, it is necessary to introduce the Gibbs phase conditions in order to calculate the properties for the coexisting phases. However, it was shown by Haar and Gallagher[1] that almost negligible error results if an explicit relation is used for the vapor pressure, P_s, obtained by separately fitting the saturated vapor pressure data of Cragoe[6] for the range from the triple point to 373K and of the mean of the data of Beattie and Lawrence[7] and of Keyes[8] above 373K. The equation so obtained is

$$\log_e \frac{P_s}{P_c} = \frac{T_c}{T} \quad (AX + BX^{3/2} + CX^{5/2} + DX^5)$$

where $X = 1 - T/T_c$

$P_c = 111.85$ atm.

$T_c = 405.4$K

$A = -7.296510$

$B = 1.618053$

$C = -1.956546$

$D = -2.114118$

Eq. (10b) and Eq. (3) define the coexisting phases for this report and all properties over the temperature-pressure range of the thermodynamic surface, subject to the low temperature boundary of the melting solid. The thermodynamic surface is consistent with the following values for the parameters at the triple point,

$T_t = 195.48$K

$P_t = .06063$ bar

$\rho_t^g = .00006382$ g/cm^3, $\rho_t^\ell = .73374$ g/cm^3,

and at the critical point,

$T_c = 405.4$K

$P_c \quad 113.04$ bar

$\rho_c = .2350$ g/cm^3

The relationship between the pressure and temperature of the melting solid was calculated by means of the Clapeyron equation. For the latent heat, the value reported by Overstreet and Giauque[9] was used; for the specific volume for the solid at the normal melting point, the value reported by McKelvey and Taylor[10] was used, and for the corresponding specific volume of the liquid the value reported by Cragoe and Harper[11] was used.

The Clapeyron equation is the relation

$$\frac{dT}{T} = \frac{u' - u}{L} \, dP, \qquad (11)$$

where the quantities u' and u are the specific volumes of the liquid and solid, respectively, and L is the latent heat of fusion. From the above data, the quantity $\frac{u' - u}{L} \simeq 4 \mathrm{x} 10^{-5}$ atm^{-1}; and Eq. (11) can be integrated to yield

$$T = T_s \exp[4 \mathrm{x} 10^{-5}(P - P_s)], \qquad (12)$$

where T_s and P_s are the triple point values. (The differences between the triple point values and those of the normal melting point are negligible.) Also, since P_s at the triple point is very small, the relationship can be simplified to

$$T = 195.48 \exp \{4 \mathrm{x} 10^{-5} \, P \text{ (atm)}\}. \qquad (13)$$

3. Computer programs.

The properties calculated from the equations presented in this report have been compared with the various thermodynamic measurements reported for ammonia in the comprehensive review in reference 1. In almost all cases the agreement is within the experimental accuracy of the data. Comparisons of results with P,ρ,T data are given here in figures 2 and 3. It was established in reference 1 that for most of the vapor phase and for the coexisting phases, the calculated enthalpies are accurate to within 0.1%.

To facilitate the application of these results we present in Appendices I through IV computer programs in FORTRAN with which the various properties of ammonia can be calculated. Four such programs are included:

The computer program in Appendix I is a general program for all the thermodynamic properties discussed in section 2 of this report, including the program for the calculation of Q of Eq. (4) and its derivatives with respect to temperature and density which are used by most of the other programs. The independent variables are either pressure and temperature or density and temperature.

The computer programs in Appendix II refer only to certain properties for the coexisting phases, including the latent heat of vaporization, the vapor pressure of the saturated liquid, the densities of the saturated vapor and of the saturated liquid and the heat capacity of the saturated fluid. The dependent variable for these is either the temperature or the corresponding pressure of the saturated liquid.

As all of the above programs assume densities in g/cm^3, temperatures in kelvins and pressure in atmospheres, a set of simple routines is presented in Appendix III for conversions back and forth between these units and other commonly used systems of units.

Appendix IV contains examples of typical calculations using the routines for Appendices I through III.

All quantities other than pressure, density and temperature are calculated and used in dimensionless units. Results in two commonly used systems of units can be obtained as follows:

To obtain heat capacities and entropy in SI units (joules/g), multiply the dimensionless quantities by 0.48820; or in Btu/lb., multiply the dimensionless quantity by 0.210027.

To obtain enthalpies, internal energies or heats of vaporization in SI units (joules/g K), multiply the dimensionless quantities by (0.48820 T) where T is in K; or in Btu/lb. deg F, multiply the dimensionless quantities by (0.210027 T) where T is in deg R.

The programs as presented are in single precision except for the coefficients of the generating function 'Q', which are in double precision. This will give accuracy to within the limits of the equation when used on most computers. (When used on computers with word lengths of 48 bits or more, even these coefficients may be used in single precision.) If more precision is needed, the following can be made double precision in all routines: T, P, D, Q01, Q02, Q10, Q20, Q11. The greater precision may be required when making calculations at liquid densities or in the vicinity of the critical point, particularly when obtaining values for the thermodynamic functions requiring higher derivatives of the generating function Q, such as, for instance, C_p. In these cases the contributions of all of the 44 terms are of importance, as there is much cancellation of contributions from individual terms.

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C
C                              APPENDIX I
C              PACKAGE OF FORTRAN PROGRAMS TO GENERATE THE THERMO-
C              DYNAMI C PROPERTIES OF AMMONIA FOR ENTIRE REGION.
C
        SUBROUTINE QQ(Q,L,K,T,D)
C  THIS IS THE GENERATING   FUNCTION FOR Q AND ITS DERIVATIVES USED IN
C  THE CALCULATION OF THE OTHER   FUNCTIONS.  Q IS GENERATED AS A FCT
C  OF T AND D. AND L IS THE ORDER OF THE DERIVATIVE OF Q WITH RESPECT
C  TO RECIPROCAL TEMP.  AND K IS THE ORDER OF THE DERIV. W.R.T. DENSITY.
      DOUBLE PRECISION A,A1,A2,DD,C,TT,QT
      DIMENSION P(5,5),DD(10),TT(7),A(44),II(44),JJ(44),A1(22),A2(22)
      EQUIVALENCE (A1(1),A(1)),(A2(1),A(23))
      DATA II/6*1,6*2,6*3,6*4,4*5,4*6,4*7,4*8,4*9/,N/44/
      DATA JJ/1,2,3,4,5,6,1,2,3,4,5,6,1,2,3,4,5,6,1,2,3,4,5,6,1,2,3,4,1,
     1 2,3,4,1,2,3,4,1,2,3,4,1,2,3,4/
      DATA P/2.,2.,3.,4.,5.,2.,4.,6.,12.,20.,3.,6.,12.,24.,60.,4.,12.,
     1 24.,48.,120.,5.,20.,60.,120.,240./
      DATA A1/-6.4530223040 5D0,-13.719926770 5D0,-8.1006203157D0,-4.88009
     16421D0,-12.0287756268D0,6.80634593D0,8.0800943676 9D0,14.356920006D
     20,-45.0529767D0,-166.18899857D0,37.90895023D0,-40.7302083337D0,
     3 1.0329948807D0,55.84395581D0,492.0166508177D0,1737.836D0,
     4 -30.87491526376 6D0,71.48353041 6D0,-8.948264632D0,-169.7777441 4D0,
     5 -1236.53237167D0,-7812.16116831 7D0/
      DATA A2/1.77954826914D0,-38.97461096D0,-66.9228588 2D0,-1.75394377532
     132D0,208.553371335D0,21348.9466D0,247.341746D0,299.98391555D0,4509
     22.08057379D0,-37980.85D0,-306.5578854 3D0,24.1165511D0,-9323.3568D0,
     342724.0985306D0,161.7910033374 6D0,-507.478070464D0,8139.470397 4D0,
     4 -27458.71063D0,-27.8216888D0,298.8129173D0,-2772.597352D0,
     5 7668.928678D0/
      Q=0.
      IF(L+K) 12,14,18
   12 RETURN
   14 U=500./T
      C=U-1.23334977 8D0
      IF(DABS(C).LT.1.D-8) C=1.D-8
      TT(1)=1.
      DO 15 I=2,7
   15 TT(I)=TT(I-1)*C
      IF(D.LT.1.E-8) D=1.E-8
      DD(1)=1.
      DO 16 I=2,10
   16 DD(I)=DD(I-1)*D
   18 DO 200 M=1,N
      I=II(M)
      J=JJ(M)
      IF(J-L-1) 200,20,30
   20 IF(L) 200,24,28
   24 QT=1.
      GO TO 50
   28 QT=P(L,L)/2.
      GO TO 50
   30 IF(L) 200,32,40
   32 QT=TT(J)
      GO TO 50
   40 QT=P(L,J-1)*TT(J-L)
   50 IF(K) 200,60,70
```

```
   60 QT=QT*DD(I)
      GO TO 100
   70 R=1.
      DO 72 MM=1,K
   72 R=R*(I-MM)
      QT=QT*R*DD(I-K)
  100 Q=Q+A(M)*QT
  200 CONTINUE
      RETURN
      END
C
        SUBROUTINE FZ(T,F0,S0,CP0,U0)
C  COMPUTES THE IDEAL GAS   FUNCTIONS AS FCT OF T: FREE ENERGY(F0/RT)
C  ENTROPY(S0/R);  CP(CP0/R);      AND INTERNAL ENERGY(U0/RT).
      DIMENSION A(12)
      DATA A/-3.872727,.64463724,3.2238759,-.0021376925,.86890833E-5,
     1 -.24085149E-7,.36893175E-10,-.35034664E-13,.20563027E-16,
     2 -.685342E-20,.99392427E-24,0./
      U=T
      IF(T.LE.10.) U=10.
      F0 =A(1)*ALOG(U)+A(2)/U+A(3)+A(4)*U+A(5)*U*U+A(6)*U**3+A(7)*U**4
     1 +A(8)*U**5+A(9)*U**6+A(10)*U**7+A(11)*U**8
      S0=A(1)*(ALOG(U)+1.) + A(3) + 2.*A(4)*U + 3.*A(5)*U*U + 4.*A(6)*U
     1**3 + 5.*A(7)*U**4 + 6.*A(8)*U**5 + 7.*A(9)*U**6 + 8.*A(10)*U**7
     2 + 9.*A(11)*U**8
      CV0=A(1)/U+2.*A(4)+6.*A(5)*U+12.*A(6)*U*U+20.*A(7)*U**3+30.*A(8)*
     1 U**4 + 42.*A(9)*U**5 + 56.*A(10)*U**6 + 72.*A(11)*U**7
      CV0=-CV0*U
      S0=-S0
      U0=S0+F0-1.
      RETURN
      END
C
        FUNCTION PRES(D,T)
C  PRES CALCULATES THE PRESSURE IN ATMOSPHERES USING D,T,Q AND DQ/D(D).
      COMMON /QQQQ/ Q00,Q01,Q02,Q10,Q20,Q11
      PRES = 4.818*T*D*(1.+D*(Q00+D*Q01))
      RETURN
      END
C
        FUNCTION DPDD(D,T)
C DPDD CALCULATES THE DERIVATIVE OF THE PRESSURE(IN ATM) WITH RESPECT
C TO DENSITY (IN GM/CC).
      COMMON /QQQQ/ Q00,Q01,Q02,Q10,Q20,Q11
      DPDD = 4.818*T*(1.+2.*D*Q00 + D*D*(4.*Q01+D*Q02))
      RETURN
      END
C
        FUNCTION ENTR(D,T,S0)
C  CALCULATES THE ENTROPY IN DIMENSIONLESS UNITS (S/R). REQUIRES
C PRIOR CALL TO FZ, Q00 AND Q10
      COMMON /QQQQ/ Q00,Q01,Q02,Q10,Q20,Q11
      U=500./T
      TD=T*D
      IF(TD.LT.1.E-6) TD=1.E-6
      ENTR=SIG+D*U*Q10-D*Q00-ALOG(4.818*TD)
      RETURN
      END
```

```
C
        FUNCTION ENTH(D.T.ENER)
C  CALCULATES THE ENTHALPY IN DIMEMSIONLESS UNITS (H/RT). REQUIRES
C  PRIOR CALL TO ENER. FZ.Q00.Q01 AND Q10.
      COMMON /QQQQ/ Q00.Q01.Q02.Q10.Q20.Q11
      ENTH=ENER + 1. + D*Q00 + D*D*Q01
      RETURN
      END
C
        FUNCTION ENER(D.T.U0)
C  CALCULATES THE INTERNAL ENERGY IN DIMENSIONLESS UNITS (U/RT).
C  REQUIRES PRIOR CALL TO FZ. Q00 AND Q10
      COMMON /QQQQ/ Q00.Q01.Q02.Q10.Q20.Q11
      U=500./T
      ENER=D*U*Q10 + U0
      RETURN
      END
C
        FUNCTION CV(D.T.CP0)
C  CALCULATES THE HEAT CAPACITY AT CONST VOLUME IN DIMENSIONLESS
C  UNITS (CV/R). REQUIRES PRIOR CALLS TO FZ. Q00 AND Q20.
      COMMON /QQQQ/ Q00.Q01.Q02.Q10.Q20.Q11
      U=500./T
      CV=CP0-1.-D*U*U*Q20
      RETURN
      END
C
        FUNCTION CP(D.T.CV)
C  CALCULATES THE HEAT CAPACITY AT CONST PRESSURE IN DIMENSIONLESS
C  UNITS (CP/R). REQUIRES PRIOR CALLS TO FZ. Q00. Q01.Q02. Q10. Q20.
C  Q11 AND CV.
      COMMON /QQQQ/ Q00.Q01.Q02.Q10.Q20.Q11
      U=500./T
      CP=(1.+D*(Q00-U*Q10+D*(Q01-U*Q11)))**2/(1.+D*(2.*Q00+D*(4.*Q01+D*
     1 Q02)))+CV
      RETURN
      END
C
         SUBROUTINE DFIND(DOUT.P.D.T.DPD)
C  THIS SUBROUTINE. BY AN ITERATIVE PROCESS USING THE FUNCTIONS
C  PRES AND DPDD. WILL CALCULATE THE DENSITY AS A FCT OF A GIVEN
C  PRESSURE AND TEMPERATURE.  THE REQUIRED INPUTS ARE P. T. AND
C  D(WHICH IS AN INITIAL GUESS FOR THE DENSITY).  THE OUTPUTS ARE
C  DOUT (THE DENSITY CONSISTANT WITH THE INPUTS P AND T) AND DPD
C  (THE VALUE OF DP/DD AT P AND T).  THE VALUES OF P ARE IN ATM.
C  T IN K. AND D AND DOUT IN G/CC.  NOTE THAT FOR T LESS THAN TC.
C  AND FOR P AND T NEAR THE COEXISTANCE CURVE. CARE MUST BE USED IN
C  THE SELECTION OF THE INITIAL GUESS FOR D SO THAT SPURIOUS VALUES
C  IN THE TWO PHASE REGION ARE NOT RETURNED.
      COMMON /QQQQ/ Q0.Q1.Q2.Q10.Q20.Q11
      DD=D
      L=0
    9 L=L+1
      IF(DD.LE.0.) DD=1.E-8
      IF(DD.GT..85) DD=.85
      CALL QQ(Q0.0.0.T.DD)
      CALL QQ(Q1.0.1.T.DD)
      CALL QQ(Q2.0.2.T.DD)
```

```
      DPDX=1.1*DPDD(DD,T)
      IF(DPDX.LT..1) DPDX=.1
      PP=PRES(DD,T)
      IF(ABS(1.-PP/P).LT.1.E-6) GO TO 20
      X=(P-PP)/DPDX
      IF(DABS(X).GT..1) X=X*.1/DABS(X)
      DD=DD+X
      IF(L.LE.20) GO TO 9
   20 CONTINUE
      DOUT=DD
      RETURN
      END
C
      SUBROUTINE PHASE(P,T,DL,DG,K)
C  THIS SUBROUTINE WILL PERFORM THE FOLLOWING FUNCTIONS:
C    1. IF P AND T ARE SUPPLIED, A VALUE OF K WILL BE RETURNED
C       OF -1,0,1,2 OR 3 WITH THE FOLL3WING MEANINGS: K=-1 IS
C       ERROR RETURN (P OR T LESS THAN 0.)    K=0 POINT (P,T) IS ON
C       COEXISTANCE CURVE AND APPROXIMATE VALUES FO3 DL AN3 DG ARE
C       CALCULATED. K=1 INDICATES T LESS THAN TC. POINT (P,T) IS
C       IN VAPOR PHASE. APPROXIMATE D=DG=DL CALCULATED.  K=2 SIM-
C       ILAR TO K=1, BUT POINT (P,T) IS IN LIQUID PHASE.  K=3
C       INDICATES T G.T. TC, AND D=DG=DL IS APPROXIMATED.
C    2. IF T LESS THAN TC AND P=0, PS(T) WILL BE CALCULATE3 ALONG
C       WITH APPROXIMATE DG AND DL. IF    LESS THAN PC AND T=0,
C       TS(P) WILL BE CALCULATED A_ONG WITH APP3OXIMATE DG AND DL.
      IF(P) 10,10,20
   10 IF(T.LT.195. .OR. T.GE.405.5) GO TO 90
   14 P=PS(T)
   16 CALL DS(T,DL,DG)
      K=0
      RETURN
   20 IF(T) 22,22,30
   22 IF(P-111.55) 24,24,90
   24 IF(P-.06) 90,26,26
   26 T=TS(P)
      GO TO 16
   30 IF(T-405.5) 32,50,50
   32 PX=PS(T)
   34 CALL DS(T,DL,DG)
      IF(P-PX) 36,14,40
   36 DG=DG*P/PX
      DL=DG
      K=1
      RETURN
   40 DG=DL
      K=2
      RETURN
   50 D=P*(.0002107-5.19D-8*P-2.289D-7*T)-1.2823D-6*T
      D=D+P/T/4.818
      IF(D.LT.1.D-5)    D=.00001
      DL=D
      DG=DL
      K=3
       RETURN
   90 DL=0.
      DG=0.
      K=-1
      RETURN
      END
```

```
C
C                             APPENDIX II
C       FORTRAN PROGRAMS FOR FUNCTIONS PERTAINING TO COEXISTANCE LINE
C
        FUNCTION PS(T)
C  PS CALCULATES THE VAPOR PRESSURE (IN ATM) AS A FCT OF T IN K.
C  FOR T GREATER THAN TC, 0. IS RETURNED.
      DIMENSION A(4)/-7.296510,1.618053,-1.956546,-2.114118/
      IF(T.GT.405.4) GO TO 10
      TH=T/405.4
      TM=1.-TH
      TS=DSQRT(TM)
      P=TM*TS
      Q=P*TM
      R=Q*Q
      F=(A(1)*TM+A(2)*P+A(3)*Q+A(4)*R)/TH
      PS=111.85*EXP(F)
      RETURN
   10 PS=0.
      RETURN
      END
C
        FUNCTION DPSDT(T)
C  CALCULATES THE DERIVATIVE OF THE VAPOR PRESSURE CURVE WITH
C RESPECT TO T.  FOR T GREATER THAN TC, THE VALUE 2.03 (THE APPROX-
C IMATE VALUE AT TC) IS RETURNED.
      DIMENSION A(4)/-7.296510,1.618053,-1.956546,-2.114118/
      IF(T.GT.405.4) GO TO 10
      TH=T/405.4
      TM=1.-TH
      TS=SQRT(TM)
      P=TM*TS
      Q=P*TM
      R=Q*Q
      F=(A(1)*TM+A(2)*P+A(3)*Q+A(4)*R)/TH
      PS=111.85*EXP(F)
      S=P*Q
      DPSDT=(-F-A(1)-1.5*A(2)*TS-2.5*A(3)*P-5.*A(4)*S)*PS/T
      RETURN
   10 DPSDT=2.03
      RETURN
      END
C
      FUNCTION TS(P)
C  CALCULATES BY AN ITERATIVE METHOD USING PS(T) AND GENERATING
C  A STARTING VALUE BY AN APPROXIMATE EQUATION. THE SATURATION TEMPERATURE
C  AS A FUNCTION OF THE PRESSURE IN ATM.  IF P LESS THAN THE TRIPLE POINT
C  VALUE OR GREATER THAN PC, 0 IS RETURNED.
      Q=1./P
      IF(P.GT..058 .AND. P.LT.111.85) GO TO 4
      TS=0.
      RETURN
    4 CONTINUE
      T = 252.10703 + P*(5.6658636 + P*( -.12457077 + P*(.00135987
     1 -P*.00000531942))) + Q*(-15.379678+Q*(1.528315-Q*.04906))
    5 PX=PS(T)
      IF(ABS(1.-P/PX).LT.1.E-5) GO TO 10
```

```
      DT=(P-PX)/DPSDT(T)
      T=T+DT
      GO TO 5
   10 TS=T
      RETURN
      END
      SUBROUTINE DS(T,DL,DG)
C  THIS SUBROUTINE WILL CALCULATE APPROXIMATE COEXISTING LIQUID
C   AND VAPOR DENSITIES AT THE TEMPERATURE SUPPLIED, USEFUL FOR
C  INITIAL GUESSES IN THE SUBROUTINE DFIND.  IF T GREATER THAN TC,
C  DL = DG = 0.
      DC=.235
      IF(T-405.4) 10,80,90
   10 DT=1.-T/405.4
       IF(T.LT.395.) GO TO 100
      T1=DT**.35
      T2=DT**.541
      T3=T2*T2
      T4=DT*2.9653
      DL=T4+T1*(2.117-1.4097*T2-.89802*T3)
      DG=T4-T1*(2.117+1.1390*T2+.57253*T3)
      DL=DC*(DL+1.)
      DG=DC*(DG+1.)
      RETURN
   80 DL=DC
      DG=DC
      RETURN
   90 DL=0.
      DG=0.
      RETURN
  100  Q=DT
       DL=.387131-.00096947/Q+Q*(1.1513875+Q*(-1.4943106+Q*1.1183325))
       DG=.0828867+.00095867/Q+Q*(-.60039534+Q*(1.4434594-Q*1.1678605))
       RETURN
      END
C
        FUNCTION HV(T,DL,DG)
C   THIS FUNCTION WILL CALCULATE THE HEAT OF VAPORIZATION IN DIM-
C   ENSIONLESS UNITS (L/RT) AT THE INPUT TEMPERATURE T.  DL AND DG
C   ARE REQUIRED TO BE PREVIOUSLY CALCULATED AND SUPPLIED AS INPUT
      U=500./T
      CALL QQ(Q0,0,0,T,DL)
      CALL QQ(Q1,0,1,T,DL)
      CALL QQ(Q2,1,0,T,DL)
      CALL QQ(R0,0,0,T,DG)
      CALL QQ(R1,0,1,T,DG)
      CALL QQ(R2,1,0,T,DG)
      HV=U*(DG*R2-DL*Q2) + DG*(R0+DG*R1) - DL*(Q0+DL*Q1)
      RETURN
      END
C
      FUNCTION CS(D,T,CPR)
C  CALCULATES THE HEAT CAPACITY OF THE SATURATES FLUID IN
C  DIMENSIONLESS UNITS (CS/R). INPUTS ARE D,T AND THE DIMENSIONLESS
C  CP/R CALCULATED PRIOR TO THE CALL.
      COMMON /QQQQ/ Q00,Q01,Q02,Q10,Q20,Q11
      TDPDT=PRES(D,T)-D*500.*4.818*D*(Q10+D*Q11)
      CS=CPR-TDPDT/DPDD(D,T)/D/D *DPSDT(T)*.101325
      RETURN
      END
```

```
      FUNCTION TK(TF)
      TK=(TF+459.67)*5./9.
      RETURN
      END
C
      FUNCTION TF(TK)
      TF=1.8*TK-459.67
      RETURN
      END
C
      FUNCTION PATM(PSIA)
      PATM=PSIA/14.696
      RETURN
      END
C
      FUNCTION PSIA(PATM)
      PSIA=PATM*14.696
      RETURN
      END
C
      FUNCTION PAT(PBAR)
      PAT=PBAR/1.01325
      RETURN
      END
C
      FUNCTION PBAR(PATM)
      PBAR=PATM*1.01325
      RETURN
      END
C
      FUNCTION DGCC(DLBCF)
      DGCC=DLBCF/62.428
      RETURN
      END
C
      FUNCTION DLBCF(DGCC)
      DLBCF=DGCC*62.428
      RETURN
      END
```

APPENDIX IV
EXAMPLES OF USE OF PROGRAMS IN ABOVE PACKAGES

THE FOLLOWING SAMPLE PROGRAM WILL CALCULATE THE DENSITY AND FIVE THERMODYNAMIC FUNCTIONS AT A POINT (P,T) SUPPLIED. P SUPPLIED IN BAR, T IN DEG C, DENSITY IN GM/CC, CP,CV,S IN JOULES/GM DEG C. AND INTERNAL ENERGY, ENTHALPY IN JOULES/GM.

```
   COMMON /QQQQ/ Q00,Q01,Q02,Q10,Q20,Q11
1  READ 2, PBAR,TC
2  FORMAT(2F10.3,F10.6,2F10.3,3F10.5)
   P=PATM(PBAR)
   IF(P.LE.0.) STOP
   T=TC+273.15
   CALL PHASE(P,T,DL,DG,K)
   IF(K.EQ.-1) GO TO 1
   CALL DFIND(D,P,DL,T,DX)
   CALL QQ(Q10,1,0,T,D)
   CALL QQ(Q20,2,0,T,D)
   CALL QQ(Q11,1,1,T,D)
   CALL FZ(T,F0,S0,CV0,E0)
   CVV=CV(D,T,CV0)
   CPP=CP(D,T,CVV)*.4882
   CVV=CVV*.4882
   S=ENTR(D,T,S0)*.4882
   E=ENER(D,T,E0)
   H=ENTH(D,T,E)*.4882*T
   E=E*.4882*T
   PRINT 2,PBAR,TC,D,H,E,S,CPP,CVV
   GO TO 1
   END
```

A SAMPLE PROGRAM TO CALCULATE THE SATURATION TEMPERATURE IN DEG F, DENSITIES IN LB/CU FT, AND HEAT OF VAPORIZATION IN BTU/LB AT A GIVEN PRESSURE IN PSIA

```
   READ 1, PSI
1  FORMAT(5F10.3)
   P=PATM(PSI)
   T=TS(P)
   CALL DS(T,XDL,XDG)
   CALL DFIND(DL,P,XDL,T,DX)
   CALL DFIND(DG,P,XDG,T,DY)
   HH=HV(T,DL,DG)*.210027*T
   DL=DLBCF(DL)
   DG=DLBCF(DG)
   PRINT 1, PSI,TT,DL,DG,HH
   STOP
   END
```

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An outline is presented of the basic results of the extensive correlation for the thermodynamic properties of ammonia recently completed at this laboratory. Computer programs are presented for the calculation of thermodynamic properties in the range including the triple point temperature to 5/3 the critical temperature and pressures from the dilute gas to 8000 bar.

17. KEY WORDS *(six to twelve entries; alphabetical order; capitalize only the first letter of the first key word unless a proper name; separated by semicolons)* Ammonia; correlation; gas; liquid; thermodynamic properties; thermodynamic surface.

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