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Guideline on the IAPWS Formulation 2001 for the Thermodynamic Properties of Ammonia-Water Mixtures

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Documentation related to the formulation contained in this guideline can be found in an article "*A Helmholtz Free Energy Formulation of the Thermodynamic Properties of the Mixture {Water + Ammonia}*" by R. Tillner-Roth and D.G. Friend [1]. This formulation provides the most accurate representation of the thermodynamic properties of the fluid phases of mixtures of ammonia and water over a wide range of conditions available at the time this guideline was prepared.

Further information about this guideline and other documents issued by IAPWS can be obtained from the Executive Secretary of IAPWS or on the IAPWS web site at http://www.iapws.org.

The IAPWS Formulation 2001 for the Thermodynamic Properties of Ammonia-Water Mixtures

1 Nomenclature

a	Coefficients in Eqs. (2), (8), and (A1)
c	Coefficients in Eq. (9)
C_V	Molar isochoric heat capacity
C_p	Molar isobaric heat capacity
d	Exponents of δ in Eq. (8) and (A1)
e	Exponents of δ in Eq. (8) and (A1)
f	Molar Helmholtz free energy
F	Thermodynamic derivative in Table 4
H	Molar enthalpy
k_T	Coefficient in Eq. (6)
k_V	Coefficient in Eq. (7)
M	Molar mass
p	Pressure
R	Molar gas constant
S	Molar entropy
t	Exponent of τ in Eqs. (2), (8), and (A1)
T	Absolute temperature (ITS-90)
U	Molar internal energy
V	Molar volume
w	Speed of sound
x	Mole fraction of ammonia
Z	Compressibility factor, $p/\rho RT$
α	Exponent in Eq. (4)
β	Exponent in Eq. (5)
γ	Exponent in Eq. (8)
δ	Reduced density
θ	Coefficients in Eq. (2)
ρ	Molar density
φ	Fugacity coefficient
Φ	Reduced Helmholtz free energy, f/RT
$\Delta\Phi$	Departure function, Eq. (8)
τ	Reduced inverse temperature

Subscripts

1	First component, water
2	Second component, ammonia
12	Combined term for mixture
BUB	Bubble point
c	Critical point
DEW	Dew point
i	Running index for coefficients
L	Liquid phase
n	Mixture residual reducing quantity
tr	Triple point
v	Vapor phase
x	Derivative with respect to composition
δ	Derivative with respect to reduced density
φ	Derivative needed for fugacity
τ	Derivative with respect to reduced density

Superscripts

o	Ideal gas
r	Residual

2 Reference Constants

The reference constants for the ammonia-water system are given in Table 1. The molar gas constant, R, used in the mixture model is 8.314 471 J mol^{-1} K^{-1} from Ref. [2].[*]

Table 1. Reference constants for pure water and pure ammonia.

Water	Ammonia
T_{c1} = 647.096 K ρ_{c1} = 322 kg m^{-3} / M_1 M_1 = 18.015 268 g mol^{-1}	T_{c2} = 405.40 K ρ_{c2} = 225 kg m^{-3} / M_2 M_2 = 17.030 26 g mol^{-1}

3 Pure Fluid Limits

The formulation was constrained to be equivalent to the thermodynamic surface described by the IAPWS Formulation 1995 for the Thermodynamic Properties of Ordinary Water Substance for General and Scientific Use [5] in the limit of pure water and to the thermodynamic surface described in Ref. [4] in the limit of pure ammonia. However, because of the small differences in the values for the molar gas constant, used in this mixture formulation and in the formulation for pure water [5], there will be small differences between pure water properties calculated from this formulation and those calculated from the formulation described in Ref. [5]; additionally, rounding associated with the introduction of a common set of reducing parameters for the ideal gas states of ammonia and water (see Eq. (2)) introduces an additional small discrepancy for both water and ammonia. These differences may amount to 1 part in 60 000. The equation for pure ammonia is summarized in the Appendix to this release.

4 The Formulation

The formulation is an equation for the molar Helmholtz free energy f which is expressed in dimensionless form, $\Phi = f/(RT)$, and separated into two parts, an ideal gas part Φ^{o} and a residual part Φ^{r}. The resulting equation is

$$\frac{f(\rho, T, x)}{RT} = \Phi = \Phi^{\mathrm{o}}(\tau^{\mathrm{o}}, \delta^{\mathrm{o}}, x) + \Phi^{r}(\tau, \delta, x) \tag{1}$$

where the gas constant R is given in Section 2, x is the mole fraction of ammonia, and the dimensionless variables are given by $\tau^{\mathrm{o}} = T^{\mathrm{o}}/T$, $\delta^{\mathrm{o}} = \rho/\rho^{\mathrm{o}}$, $\tau = T_{\mathrm{n}}(x)/T$, and $\delta = \rho/\rho_{\mathrm{n}}(x)$ with the

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[*] This differs slightly from the current CODATA recommended value [3], R = 8.314 472 J mol^{-1} K^{-1}, but agrees with the value adopted in Ref. [4] for the thermodynamic surface of ammonia.

constants, T^{o} and ρ^{o}, and functions of composition, $T_{\mathrm{n}}(x)$ and $\rho_{\mathrm{n}}(x)$, given below.

The ideal gas contribution was evaluated by using the ideal gas expressions for pure ammonia and pure water as given in Refs. [4] and [5], respectively, and the standard thermodynamic expression for the ideal gas Helmholtz energy of binary mixtures. The expression for Φ^{o} is

$$\Phi^{\mathrm{o}}\left(\tau^{\mathrm{o}},\delta^{\mathrm{o}},x\right)=\ln\delta^{\mathrm{o}}+(1-x)\{a_1^{\mathrm{o}}+a_2^{\mathrm{o}}\tau^{\mathrm{o}}+a_3^{\mathrm{o}}\ln\tau^{\mathrm{o}}+\ln(1-x)+\sum_{i=4}^{8}a_i^{\mathrm{o}}\ln[1-\exp(-\theta_i\tau^{\mathrm{o}})]\}+$$
$$x\{a_9^{\mathrm{o}}+a_{10}^{\mathrm{o}}\tau^{\mathrm{o}}+a_{11}^{\mathrm{o}}\ln\tau^{\mathrm{o}}+\ln(x)+\sum_{i=12}^{14}a_i^{\mathrm{o}}(\tau^{\mathrm{o}})^{t_i}\}. \tag{2}$$

The coefficients in the pure fluid equations were adjusted so that the same reduced temperature and density could be used in all terms of the mixture ideal gas expression; thus T^{o} = 500 K and ρ^{o}= 15 mol dm^{-3}, and the coefficients are given in Table 2. In this work, we have adjusted the coefficients a^{o}_i, i = 1,2,9,10 so that the internal energy and entropy are 0 for each pure fluid at its triple point temperature in the saturated liquid.

Table 2. Coefficients of the ideal part of the Helmholtz free energy.

i	a_i^{o}	θ_i	i	a_i^{o}	t_i
1	-7.720 435	–	9	-16.444 285	–
2	8.649 358	–	10	4.036 946	–
3	3.006 320	–	11	-1.0	–
4	0.012 436	1.666	12	10.699 55	1/3
5	0.973 15	4.578	13	-1.775 436	-3/2
6	1.279 500	10.018	14	0.823 740 34	-7/4
7	0.969 560	11.964			
8	0.248 730	35.600			

The residual contribution to the free energy is given by

$$\Phi^{\mathrm{r}}(\tau,\delta,x)=(1-x)\Phi_1^{\mathrm{r}}(\tau,\delta)+x\Phi_2^{\mathrm{r}}(\tau,\delta)+\Delta\Phi^{\mathrm{r}}(\tau,\delta,x) \tag{3}$$

where Φ^{r}_1 is the residual part of the reduced Helmholtz energy of water from Ref. [5], Φ^{r}_2 is the residual part of the reduced Helmholtz energy of ammonia from Ref. [4] (see also the Appendix), and $\Delta\Phi^{\mathrm{r}}$ is an empirical departure function for the mixture.

The reducing functions used to define τ and δ in Eq. (3) are given by

$$T_{\mathrm{n}}(x)=(1-x)^2T_{\mathrm{c1}}+x^2T_{\mathrm{c2}}+2x(1-x^{\alpha})T_{\mathrm{c12}} \tag{4}$$

and

$$\frac{1}{\rho_{\mathrm{n}}(x)} = (1-x)^2\left(\frac{1}{\rho_{\mathrm{c1}}}\right) + x^2\left(\frac{1}{\rho_{\mathrm{c2}}}\right) + 2x(1-x^{\beta})\left(\frac{1}{\rho_{\mathrm{c12}}}\right) \tag{5}$$

where

$$T_{\mathrm{c12}} = \frac{k_T}{2}(T_{\mathrm{c1}} + T_{\mathrm{c2}}) \tag{6}$$

and

$$\frac{1}{\rho_{\mathrm{c12}}} = \frac{k_V}{2}\left(\frac{1}{\rho_{\mathrm{c1}}} + \frac{1}{\rho_{\mathrm{c2}}}\right). \tag{7}$$

Finally, the last term of Eq. (3) is given by

$$\frac{\Delta\Phi^{\mathrm{r}}(\tau,\delta,x)}{x(1-x^{\gamma})} = a_1\tau^{t_1}\delta^{d_1} + \sum_{i=2}^{6} a_i\tau^{t_i}\delta^{d_i}\exp(-\delta^{e_i}) + x\sum_{i=7}^{13} a_i\tau^{t_i}\delta^{d_i}\exp(-\delta^{e_i}) + a_{14}x^2\tau^{t_{14}}\delta^{d_{14}}\exp(-\delta^{e_{14}}). \tag{8}$$

All of the coefficients, parameters, and exponents of Eqs. (4)-(8) are given in Table 3.

Table 3. Coefficients of the reducing functions and the departure function.

Reducing functions									
k_T = 0.964 840 7			k_V = 1.239 511 7		α = 1.125 455			β = 0.897 806 9	
Departure Function									
γ = 0.524 837 9									
i	a_i	t_i	d_i	e_i	i	a_i	t_i	d_i	e_i
1	-1.855 822E-02	3/2	4	--	8	-1.368 072E-08	4	15	1
2	5.258 010E-02	1/2	5	1	9	1.226 146E-02	7/2	4	1
3	3.552 874E-10	13/2	15	1	10	-7.181 443E-02	0	5	1
4	5.451 379E-06	7/4	12	1	11	9.970 849E-02	-1	6	2
5	-5.998 546E-13	15	12	1	12	1.058 408 6E-03	8	10	2
6	-3.687 808E-06	6	15	2	13	-0.196 368 7	15/2	6	2
7	0.258 619 2	-1	4	1	14	-0.777 789 7	4	2	2

5 Relations of Thermodynamic Properties to the Dimensionless Helmholtz Free Energy

All thermodynamic properties of fluid mixtures of ammonia and water can be derived from Eqs.(1) –(8) by using the appropriate combinations of the ideal-gas part Φ^{o} and the residual part Φ^{r} of the dimensionless Helmholtz free energy and their derivatives. Relations between the thermodynamic properties and Φ^{o} and Φ^{r} and their derivatives are summarized in Table 4.

Table 4. Relations of Thermodynamic Properties to the ideal-gas part Φ^{o} and the residual part Φ^{r} of the dimensionless Helmholtz free energy and their derivatives.

Property	Relation
Compressibility Factor	$Z = \dfrac{p(\tau,\delta,x)V}{RT} = 1 + \delta\Phi_{\delta}^{\mathrm{r}}$
Internal Energy	$\dfrac{U(\tau,\delta,\tau^{\mathrm{o}},\delta^{\mathrm{o}},x)}{RT} = \tau^{\mathrm{o}}\Phi_{\tau^{\mathrm{o}}}^{\mathrm{o}} + \tau\Phi_{\tau}^{\mathrm{r}}$
Enthalpy	$\dfrac{H(\tau,\delta,\tau^{\mathrm{o}},\delta^{\mathrm{o}},x)}{RT} = 1 + \delta\Phi_{\delta}^{\mathrm{r}} + \tau^{\mathrm{o}}\Phi_{\tau^{\mathrm{o}}}^{\mathrm{o}} + \tau\Phi_{\tau}^{\mathrm{r}}$
Entropy	$\dfrac{S(\tau,\delta,\tau^{\mathrm{o}},\delta^{\mathrm{o}},x)}{R} = \tau^{\mathrm{o}}\Phi_{\tau^{\mathrm{o}}}^{\mathrm{o}} + \tau\Phi_{\tau}^{\mathrm{r}} - \Phi^{\mathrm{o}} - \Phi^{\mathrm{r}}$
Isochoric Heat Capacity	$\dfrac{C_V(\tau,\delta,\tau^{\mathrm{o}},\delta^{\mathrm{o}},x)}{R} = -\tau^{\mathrm{o}2}\Phi_{\tau^{\mathrm{o}}\tau^{\mathrm{o}}}^{\mathrm{o}} - \tau^{2}\Phi_{\tau\tau}^{\mathrm{r}}$
Isobaric Heat Capacity	$\dfrac{C_p(\tau,\delta,\tau^{\mathrm{o}},\delta^{\mathrm{o}},x)}{R} = \dfrac{C_V}{R} + \dfrac{\left[1 + \delta\Phi_{\delta}^{\mathrm{r}} - \delta\tau\Phi_{\delta\tau}^{\mathrm{r}}\right]^2}{\left[1 + 2\delta\Phi_{\delta}^{\mathrm{r}} + \delta^{2}\Phi_{\delta\delta}^{\mathrm{r}}\right]}$
Speed of Sound	$\dfrac{w^2(\tau,\delta,\tau^{\mathrm{o}},\delta^{\mathrm{o}},x)M}{RT} = 1 + 2\delta\Phi_{\delta}^{\mathrm{r}} + \delta^{2}\Phi_{\delta\delta}^{\mathrm{r}} + \dfrac{\left[1 + \delta\Phi_{\delta}^{\mathrm{r}} - \delta\tau\Phi_{\delta\tau}^{\mathrm{r}}\right]^2}{C_V/R}$
Fugacity of Components	$\ln[Z\varphi_1(\tau,\delta,x)] = \Phi^{\mathrm{r}} + \delta\Phi_{\delta}^{\mathrm{r}} - xF_{\varphi}$ $\ln[Z\varphi_2(\tau,\delta,x)] = \Phi^{\mathrm{r}} + \delta\Phi_{\delta}^{\mathrm{r}} + (1-x)F_{\varphi}$

Abbreviations:

$\Phi_{\tau^{\mathrm{o}}}^{\mathrm{o}} = \left(\dfrac{\partial\Phi^{\mathrm{o}}}{\partial\tau^{\mathrm{o}}}\right)_{\delta^{\mathrm{o}},x}$	$\Phi_{\tau^{\mathrm{o}}\tau^{\mathrm{o}}}^{\mathrm{o}} = \left(\dfrac{\partial^2\Phi^{\mathrm{o}}}{\partial\tau^{\mathrm{o}2}}\right)_{\delta^{\mathrm{o}},x}$	$\Phi_{\tau}^{\mathrm{r}} = \left(\dfrac{\partial\Phi^{\mathrm{r}}}{\partial\tau}\right)_{\delta,x}$	$\Phi_{\tau\tau}^{\mathrm{r}} = \left(\dfrac{\partial^2\Phi^{\mathrm{r}}}{\partial\tau^2}\right)_{\delta,x}$
$\Phi_{\delta}^{\mathrm{r}} = \left(\dfrac{\partial\Phi^{\mathrm{r}}}{\partial\delta}\right)_{\tau,x}$	$\Phi_{\delta\tau}^{\mathrm{r}} = \left(\dfrac{\partial^2\Phi^{\mathrm{r}}}{\partial\delta\partial\tau}\right)_{x}$	$\Phi_{\delta\delta}^{r} = \left(\dfrac{\partial^2\Phi^{\mathrm{r}}}{\partial\delta^2}\right)_{\tau,x}$	$\Phi_{x}^{r} = \left(\dfrac{\partial\Phi^{\mathrm{r}}}{\partial x}\right)_{\delta,\tau}$

$$F_{\varphi} = \Phi_{x}^{\mathrm{r}} - \frac{\delta}{\rho_{\mathrm{n}}}\frac{d\rho_{\mathrm{n}}}{dx}\Phi_{\delta}^{\mathrm{r}} + \frac{\tau}{T_{\mathrm{n}}}\frac{dT_{\mathrm{n}}}{dx}\Phi_{\tau}^{\mathrm{r}} \qquad M = (1-x)M_1 + xM_2$$

In addition to properties in the single-phase regions, the formulation also can be used to calculate properties on the liquid-vapor (dew point and bubble point) equilibrium curves. The fugacity coefficients listed in Table 4 can be used for phase equilibrium calculations using standard thermodynamic iteration techniques.

6 Range of Validity

The thermodynamic surface covers the thermodynamic space between the solid-liquid-vapor boundary and the critical locus. It is also valid in the vapor and liquid phases for pressures up to 40 MPa (at subcritical temperatures).

The solid-liquid-vapor boundary (line of triple points) has three eutectic points, and can be described by the piecewise function discussed in Ref. [6]. The expression for temperature is

$$\begin{aligned}
&0 \le x \le 0.333\,67: \ \frac{T_{\mathrm{tr}}(x)}{273.16\ \mathrm{K}} - 1 = c_{11}x + c_{12}x^2 + c_{13}x^7 \\
&0.333\,67 < x \le 0.583\,96: \ \frac{T_{\mathrm{tr}}(x)}{193.549\ \mathrm{K}} - 1 = c_{21}(x - 0.5)^2 \\
&0.583\,96 < x \le 0.814\,73: \ \frac{T_{\mathrm{tr}}(x)}{194.380\ \mathrm{K}} - 1 = c_{31}(x - 2/3)^2 + c_{32}(x - 2/3)^3 \\
&0.814\,73 < x \le 1: \ \frac{T_{\mathrm{tr}}(x)}{195.495\ \mathrm{K}} - 1 = c_{41}(1 - x) + c_{42}(1 - x)^4
\end{aligned} \tag{9}$$

and the coefficients are given in Table 5. The pressure along this line can be determined from the formulation given in Section 4.

Table 5. Coefficients for expression for line of triple points

c_{11} = -0.343 982 3	c_{12} = -1.327 427 1
c_{13} = -274.973	c_{21} = -4.987 368
c_{31} = -4.886 151	c_{32} = 10.372 98
c_{41} = -0.323 998	c_{42} = -15.875 60

The upper limit of validity, the critical locus, can be found using the phase equilibrium criteria within the context of the present formulation. However, there may be convergence problems when an implementation of the formulation is used to calculate the critical line. Additional information about the critical region can be found in Ref. [7]. This classical formulation does not give the theoretically predicted behavior in the immediate vicinity of the critical point. Because there are very few data for the critical locus, and these data are inconsistent, there is significant uncertainty in the location of the critical locus.

Experimental data in the single-phase region are restricted to subcritical temperatures, for the liquid below 420 K and 40 MPa and for the vapor for pressures below 10 MPa. No experimental data were available for supercritical temperatures. Extrapolation into the supercritical region gives reasonable results, but the accuracy in these regions is unknown.

7 Estimates of Uncertainty

The uncertainty of coexisting liquid and vapor mole fractions calculated with this formulation is estimated to be 0.01, except in the region of the critical locus where it can increase to 0.04. Enthalpies and densities show reasonable behavior on the entire two-phase envelope, although experimental data for these properties are available only in a limited range of temperature and composition [1]. In the single-phase region, uncertainties are estimated as 1% for vapor density, 2% for liquid density, and 200 J/mol for the excess enthalpy in the region described above. However, the locus of density maxima near the melting line is not well described by this formulation. Also, improvements in the ability to describe caloric properties may be possible by explicitly incorporating speciation equilibria in the thermodynamic model [8].

8 Computer Program Verification

Tables 6 to 8 give values of thermodynamic properties at various state points in order to verify implementations of this guideline. The numbers of digits given in Tables 7 and 8 reflect adequate agreement with this guideline when alternative implementations with different iterative methods and tolerances are used for the calculation of phase boundaries.

Table 6. Property values at selected points in the single-phase region.

x -	T K	ρ mol dm^{-3}	f J mol^{-1}	p MPa	C_V J mol^{-1} K^{-1}	w m s^{-1}
0.1	600	35	-13 734.176 3	32.122 133 3	53.315 954 4	883.925 596
0.1	600	4	-16 991.669 7	12.772 109 0	52.764 455 3	471.762 394
0.5	500	32	-12 109.536 9	21.320 815 9	58.007 734 6	830.295 833
0.5	500	1	-18 281.302 0	3.642 308 0	36.822 809 8	510.258 362
0.9	400	30	-6 986.486 9	22.283 079 7	51.807 241 5	895.748 711
0.9	400	0.5	-13 790.627 8	1.549 970 8	32.970 387 0	478.608 147

Table 7. Property values at selected points on saturation boundary: bubble points.

x_L -	T K	p_{BUB} MPa	x_v -	ρ_L mol dm^{-3}	ρ_v mol dm^{-3}
0.2	300	0.040 710	0.936 0	51.941	0.016 40
0.4	400	2.554 5	0.936 3	43.318	0.860 8
0.6	500	16.698	0.784 4	25.459	8.86

Table 8. Property values at selected points on saturation boundary: dew points.

x_v -	T K	p_{DEW} MPa	x_L -	ρ_L mol dm^{-3}	ρ_v mol dm^{-3}
0.2	300	0.004 370 62	0.010 672	55.164 34	0.001 755 06
0.4	400	0.394 694	0.051 541	50.831 87	0.122 658
0.6	500	6.526 07	0.221 35	39.937 14	2.007 30

9 References

[1] R. Tillner-Roth and D.G. Friend, J. Phys. Chem. Ref. Data **27**, 63 (1998).

[2] M.R. Moldover, J.P.M. Trusler, T.J. Edwards, J.B. Mehl, and R.S. Davis, J. Res. National Bur. Stand. **93**, 85 (1988).

[3] P.J. Mohr and B.N. Taylor, J. Phys. Chem. Ref. Data **28**, 1713 (1999).

[4] R. Tillner-Roth, F. Harms-Watzenberg, and H.D. Baehr, *Eine neue Fundamentalgleichung für Ammoniak*, Proc. 20th DKV-Tagung Heidelberg, Germany, Vol. **II,** 167 (1993); H.D. Baehr and R. Tillner-Roth, *Thermodynamische Eigenschaften umweltverträglicher Kältemittel/Thermodynamic Properties of Environmentally Acceptable Refrigerants*, Springer-Verlag, Berlin (1995).

[5] Release on the IAPWS Formulation 1995 for the Thermodynamic Properties of Ordinary Water Substance for General and Scientific Use. Available from Dr. R. B. Dooley, Executive Secretary of IAPWS, Electric Power Research Institute, 3412 Hillview Avenue, Palo Alto, CA 94304-1395; W. Wagner and A. Pruss, J. Phys. Chem. Ref. Data (to be submitted, 2001).

[6] R. Tillner-Roth and D.G. Friend, J. Phys. Chem. Ref. Data **27**, 45 (1998).

[7] J. C. Rainwater and R. Tillner-Roth, in *Steam, Water and Hydrothermal Systems: Physics and Chemistry Meeting the Needs of Industry, Proc. 13th Int. Conf. on the Properties of Water and Steam*, P.R. Tremaine, P.G. Hill, D.E. Irish, and P.V. Balakrishnan, eds., NRC Research Press, Ottawa (2000); pp. 110-117.

[8] K. Thomsen and P. Rasmussen, in *Steam, Water and Hydrothermal Systems: Physics and Chemistry Meeting the Needs of Industry, Proc. 13th Int. Conf. on the Properties of Water and Steam*, P.R. Tremaine, P.G. Hill, D.E. Irish, and P.V. Balakrishnan, eds., NRC Research Press, Ottawa (2000); pp. 118-125.

10 Appendix: Thermodynamic Surface for Pure Ammonia

The thermodynamic surface for pure ammonia is taken from Ref. [4]. The ideal gas portion of this formulation is already included in Eq. (2), above. The reduced residual Helmholtz energy is given by

$$\Phi_2{}^{\mathrm{r}}(\tau,\delta) = \sum_{i=1}^{5} a_i \tau^{t_i} \delta^{d_i} + \sum_{i=6}^{21} a_i \tau^{t_i} \delta^{d_i} \exp(-\delta^{e_i}) \tag{A1}$$

with the coefficients given in Table A1.

Table A1. Coefficients for the residual portion of the Helmholtz free energy of pure ammonia.

i	a_i	t_i	d_i	e_i	i	a_i	t_i	d_i	e_i
1	-1.858 814 0E+00	1.5	1	-	12	2.397 852 0E-02	3	1	2
2	4.554 431 0E-02	-0.5	2	-	13	-4.085 375 0E-02	6	1	2
3	7.238 548 0E-01	0.5	1	-	14	2.379 275 0E-01	8	2	2
4	1.229 470 0E-02	1	4	-	15	-3.548 972 0E-02	8	3	2
5	2.141 882 0E-11	3	15	-	16	-1.823 729 0E-01	10	2	2
6	-1.430 020 0E-02	0	3	1	17	2.281 556 0E-02	10	4	2
7	3.441 324 0E-01	3	3	1	18	-6.663 444 0E-03	5	3	3
8	-2.873 571 0E-01	4	1	1	19	-8.847 486 0E-03	7.5	1	3
9	2.352 589 0E-05	4	8	1	20	2.272 635 0E-03	15	2	3
10	-3.497 111 0E-02	5	2	1	21	-5.588 655 0E-04	30	4	3
11	1.831 117 0E-03	5	8	2					