

Supplementary Materials

Table 1s. Geometries of dissociation species^{a)} standard entropy^{b)}, dipole moment,^{c)} harmonic vibrational frequencies^{d)} ω in cm^{-1} (unscaled) and IR intensities in km mol^{-1} in parentheses. B3LYP/pVDZ level of theory.

ER_n	R(E-R), $\text{\AA}$	R-E-R	$S^0_{(298)},$ $\text{J mol}^{-1} \text{K}^{-1}$	μ, D	ω_1	ω_2	ω_3	ω_4
HCl	1.290		186.7	1.31	2959 (25)			
Exp.	1.275		186.9	1.08				
$\text{GaN } ^1\Sigma^+$	1.716		223.3	3.80	804 (2)			
$\text{GaN } ^3\Pi$	1.860		234.7	2.27	608 (12)			
Exp.			226.0					
$\text{NH } ^3\Sigma^-$	1.051		181.2	1.56	3227 (32)			
Exp.	1.036		181.2					
NH_2	1.037	101.2	194.9	1.90	1532 (12)	3324 (11)	3407 (9)	
Exp.	1.024	103.3	195.0		1497	3219	3301	
NH_3	1.023	105.1	192.5	1.76	1065 (118)	1657 (9)	3442 (0.3)	3559 (0)
Exp.	1.012	106.7	192.45	1.47	950	1627	3337	3444
GaCl	2.233		239.8	2.06	372 (77)			
Exp.	2.202		240.3					
GaCl_2	2.193	119.2	303.2	1.67	114 (4)	354 (18)	408 (77)	
GaCl_3	2.138	120.0	325.8	0	127 (7)	135 (12)	367 (0)	464 (77)
Exp.	2.101	120.0	325.1	0	128	145	382	450

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a) Experimental structural data are taken from: Hargittai, M. *Chem. Rev.* **2000**, *100*, 2233;

Handbook of Chemistry and Physics, 75th ed.: Lide, D.R., Ed.; CRC Press: Boca Raton, FL, 1995.

b) Experimental thermochemical data are taken from: Wagman, D.D.; Evans, W.H.; Parker, V.B.; Shumm, R.H.; Halow, I.; Balley, S.M.; Churney, K.L.; Nuttall, R.L. The NBS Tables of Thermodynamic Properties, *J. Phys. Chem. Ref. Data*, **1982**, *11*, Suppl. 2.

c) Experimental dipole moments are taken from: Handbook of Chemistry and Physics, 75th ed.: Lide, D.R., Ed.; CRC Press: Boca Raton, FL, 1995.

d) Experimental vibrational frequencies are taken from: Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed.; Wiley: New York, 1986. Calculated, and observed vibrational frequencies are related through the equation $\nu_{\text{obs}} = 0.9461\omega_{\text{calcd}} + 22.1 \text{ cm}^{-1}$ (ref. 13).

Table 2s. Harmonic vibrational frequencies ω , cm^{-1} and IR intensities I , km mol^{-1} of investigated compounds. B3LYP/pVDZ level of theory, unscaled.

	ω , cm^{-1}	I , km mol^{-1}	ω , cm^{-1}	I , km mol^{-1}	ω , cm^{-1}	I , km mol^{-1}
GaCl	371.9	77.0				
GaCl ₂	114.0	4.2	354.1	18.3	408.2	76.9
GaCl ₃	126.9	7.2	126.9	7.2	135.4	12.4
	367.4	0.0	463.9	77.3	463.9	77.3
Cl ₃ GaNH ₃	104.3	0.0	110.5	7.7	110.5	7.7
	131.0	0.7	131.0	0.7	150.8	26.3
	356.5	10.1	380.1	7.2	423.8	63.9
	423.8	63.9	646.6	54.6	646.6	54.6
	1201.7	211.3	1609.9	22.8	1609.9	22.8
	3441.2	25.2	3568.1	59.3	3568.1	59.3
[Cl ₃ GaNH ₃] ₂	34.7	0.9	48.1	0.0	51.3	6.2
	52.5	4.3	56.2	5.4	63.0	0.0
	118.8	0.0	134.7	16.7	136.1	0.8
	147.4	40.5	152.0	0.4	156.3	0.0
	162.8	59.7	163.4	5.2	182.7	19.2
	183.7	0.0	200.5	0.2	202.6	0.1
	374.7	0.1	377.0	26.9	414.4	0.6
	423.3	148.1	435.3	33.0	436.6	0.0
	447.5	186.1	448.5	0.6	769.4	147.6
	772.7	41.3	773.9	113.7	782.7	2.9
	1425.5	0.0	1425.7	378.5	1747.8	0.0
	1750.6	52.1	1763.5	0.0	1765.8	185.4
	3633.8	0.5	3636.7	222.8	3733.9	0.9
	3735.6	189.8	3777.6	0.5	3777.7	288.4
Cl ₂ GaNH ₂	88.5	135.4	126.8	7.1	146.7	3.4
	189.9	46.6	373.0	0.0	392.9	14.8
	450.4	69.1	730.9	76.4	738.7	61.3

	1496.7	23.4	3585.2	45.9	3697.6	48.7
$[\text{Cl}_2\text{GaNH}_2]_2$	30.0	3.8	58.1	0.0	75.2	0.0
	91.9	0.0	118.8	19.7	119.8	19.8
	132.1	0.0	162.3	0.0	191.9	0.1
	219.9	0.0	378.4	49.3	402.1	0.0
	419.8	0.0	435.5	0.0	436.8	103.0
	462.4	102.1	506.2	56.3	573.5	0.0
	575.8	0.0	668.2	137.0	813.3	0.0
	851.0	0.0	876.8	0.0	894.8	325.5
	1534.4	96.7	1546.7	0.0	3486.0	83.7
	3486.8	0.0	3564.4	0.0	3564.5	86.5
$[\text{Cl}_2\text{GaNH}_2]_3$	11.7	2.0	33.1	2.5	42.1	0.8
	62.5	0.2	73.6	2.4	82.1	2.5
	84.7	0.0	94.7	4.5	98.1	2.5
	110.9	15.5	122.0	26.9	125.2	3.6
	135.6	2.3	142.5	11.2	155.7	2.0
	164.1	0.5	167.1	0.5	198.6	0.1
	376.4	45.8	380.6	60.1	390.5	6.4
	428.3	13.3	432.1	45.8	432.3	85.6
	457.8	16.6	465.4	6.3	471.4	34.2
	542.0	9.7	554.0	80.8	562.3	98.1
	583.7	37.5	604.4	46.2	640.9	163.8
	929.0	1.8	956.0	7.6	977.6	3.6
	993.7	67.1	1001.3	307.1	1029.2	187.9
	1538.4	54.6	1550.8	34.6	1560.1	39.3
	3436.2	32.0	3455.0	51.5	3456.1	26.2
	3513.5	57.0	3523.8	20.0	3524.2	61.4
$\text{NH}_3 \cdot \text{Cl}_2\text{GaNH}_2$	106.7	7.7	120.8	1.5	126.8	8.7
	127.4	0.9	137.3	5.0	176.7	27.8
	191.2	10.9	355.7	14.2	374.7	6.4
	404.1	68.4	559.9	179.7	626.3	54.0

	627.3	30.8	668.3	40.5	818.2	42.8
	1173.9	218.5	1544.0	20.5	1611.6	20.5
	1613.3	22.0	3446.5	18.0	3516.7	9.3
	3576.8	54.2	3578.4	51.3	3602.4	10.9
Ga ₂ Cl ₅ NH ₂ , C _{2v}	19.9	1.5	59.5	1.6	86.6	0.4
(bridging NH ₂)	101.1	3.1	110.4	3.1	112.5	5.2
	133.9	13.4	140.2	7.8	175.3	3.8
	183.1	1.8	195.1	2.8	217.4	62.6
	312.1	32.1	389.3	58.5	412.0	31.7
	443.8	59.0	480.3	188.9	491.1	50.0
	514.6	17.0	625.9	53.1	696.4	47.4
	802.1	41.8	890.2	0.9	929.1	182.9
	1536.4	37.9	1542.5	26.8	3471.8	40.3
	3535.0	24.8	3550.6	45.4	3626.8	24.2
NH ₃ *Cl ₂ GaNH ₂ *GaCl ₃	21.2	0.6	36.3	1.2	39.3	4.4
	69.5	0.0	73.6	7.8	81.4	0.1
	103.5	15.9	119.8	2.2	121.1	11.3
	129.7	1.5	143.4	3.5	149.7	37.2
	160.2	0.1	191.3	0.9	342.2	12.2
	351.8	17.1	380.2	15.2	414.1	65.9
	418.0	52.7	438.5	50.9	441.8	39.8
	560.7	39.8	601.7	23.0	622.9	82.4
	639.9	103.8	937.6	3.2	941.6	211.0
	1215.0	214.7	1534.2	29.7	1609.4	20.5
	1623.1	19.3	3438.0	27.0	3455.0	26.4
	3540.0	36.2	3554.7	58.4	3566.0	45.6
Cl ₃ GaNH ₃ *HCl*Cl ₂ GaNH ₂	24.2	0.6	33.0	2.7	40.4	0.4
	41.5	7.3	53.5	1.0	56.4	0.9
	77.4	0.9	82.1	0.6	104.7	7.2
	121.5	27.7	129.7	2.5	131.4	6.0
	137.1	50.2	157.4	7.1	164.5	9.1

	173.9	25.1	175.7	10.7	192.5	8.3
	265.0	103.5	346.4	7.8	374.2	22.6
	396.9	64.7	416.7	31.5	426.6	88.4
	432.9	30.5	443.2	55.6	470.3	53.1
	533.6	53.4	713.1	37.9	723.2	77.0
	741.0	43.9	770.6	66.5	1294.1	125.2
	1507.3	11.8	1607.0	22.2	1621.7	73.5
	2588.1	882.1	3371.9	236.1	3473.0	94.6
	3542.9	98.0	3547.9	150.7	3670.4	102.9
ClGaNH, ¹ A'	136.3	16.9	219.5	25.6	417.3	30.3
	767.8	87.1	865.1	20.0	3472.8	17.3
ClGaNH, ³ A''	125.2	54.9	139.2	2.0	371.6	48.8
	460.0	17.1	752.7	99.4	3360.2	2.9
[ClGaNH] ₂	48.7	0.4	87.4	5.9	118.6	0.0
	121.5	0.0	212.5	0.0	227.0	84.0
	237.5	0.0	414.1	61.9	469.7	0.0
	493.9	114.8	556.6	0.0	647.3	222.3
	698.3	130.9	795.1	0.0	895.7	0.0
	968.4	121.8	3670.2	92.8	3670.7	0.0
[ClGaNH] ₃	43.8	1.1	65.9	0.0	65.9	0.0
	84.1	5.1	84.1	5.1	118.0	0.0
	154.2	2.2	154.2	2.2	164.2	0.0
	164.2	0.0	213.4	0.0	232.7	61.9
	414.9	114.6	414.9	114.6	444.8	0.0
	469.6	0.0	469.6	0.0	527.6	189.1
	600.2	41.4	600.2	41.4	601.4	0.0
	768.6	0.0	802.5	235.5	802.5	235.5
	1041.0	0.0	1081.9	178.7	1081.9	178.7
	3596.4	0.0	3596.9	65.4	3596.9	65.4
[ClGaNH] ₄	57.7	0.0	57.7	0.0	76.2	5.0
	76.2	5.0	76.2	5.0	109.7	0.0

	109.7	0.0	109.7	0.0	201.7	2.6
	201.7	2.6	201.7	2.6	203.0	0.0
	203.0	0.0	238.6	0.0	403.0	0.0
	403.0	0.0	403.0	0.0	423.7	46.6
	423.7	46.6	423.7	46.6	476.2	0.0
	518.9	0.0	518.9	0.0	551.9	240.5
	551.9	240.5	551.9	240.5	597.5	0.9
	597.5	0.9	597.5	0.9	697.5	0.0
	807.1	0.0	807.1	0.0	807.1	0.0
	847.2	0.0	847.2	0.0	874.5	274.3
	874.5	274.3	874.5	274.3	3576.7	0.0
	3577.1	47.3	3577.1	47.3	3577.1	47.3
[ClGaNH] ₆	49.9	0.6	50.1	0.7	55.5	0.0
	62.3	0.0	68.4	0.0	69.9	0.0
	72.2	7.7	80.1	9.7	81.4	9.6
	99.8	0.0	100.4	0.0	104.1	0.0
	112.9	0.0	113.2	0.0	147.9	0.3
	149.3	0.3	180.6	1.0	181.0	0.0
	203.7	0.0	204.2	0.0	218.6	0.0
	218.8	0.0	223.1	3.5	223.3	3.6
	381.6	0.0	381.9	0.0	399.2	24.1
	399.3	25.4	407.7	57.2	416.9	0.0
	417.1	0.0	427.6	126.3	427.8	127.2
	445.7	0.0	464.6	69.5	464.8	0.0
	498.4	235.3	513.4	0.0	516.8	0.0
	560.5	92.4	561.0	95.1	590.6	0.0
	609.8	0.0	665.0	346.2	666.7	342.7
	674.6	0.0	675.3	0.0	677.1	0.5
	798.0	20.7	800.8	0.0	803.2	18.0
	806.4	0.0	817.7	0.0	837.2	446.4
	949.0	0.0	974.2	2.4	982.4	357.2

	983.6	353.3	993.4	0.0	994.6	0.0
	3526.4	86.3	3526.7	0.0	3527.2	88.9
	3527.6	0.0	3527.7	0.0	3527.8	76.0
Cl ₉ Ga ₆ N ₆ H ₉	50.5	0.0	53.8	0.0	55.0	1.1
	55.0	1.1	59.9	0.4	59.9	0.4
	71.4	2.6	76.0	0.5	76.0	0.5
	87.7	1.4	87.7	1.4	91.0	6.4
	94.9	12.6	94.9	12.6	109.0	0.3
	109.0	0.3	113.5	0.0	134.0	0.2
	134.0	0.2	138.0	12.2	141.9	10.5
	141.9	10.5	145.2	0.0	151.4	0.2
	151.4	0.2	161.2	3.6	183.1	0.0
	191.5	0.2	191.5	0.2	212.2	0.3
	242.5	0.2	242.5	0.2	268.2	12.4
	357.2	63.4	357.2	63.4	374.1	0.0
	414.4	92.1	414.4	92.1	421.5	11.6
	421.5	11.6	423.3	132.4	444.3	38.0
	457.0	17.4	457.0	17.4	474.1	10.1
	474.1	10.1	486.7	8.4	510.0	0.5
	519.5	0.0	547.7	49.2	547.7	49.2
	556.0	0.0	564.6	56.4	564.6	56.4
	604.5	0.1	604.5	0.1	633.1	229.3
	633.1	229.3	637.5	253.1	704.8	171.9
	912.5	0.0	956.3	65.0	956.3	65.0
	974.1	0.0	1003.8	149.7	1003.8	149.6
	1018.5	5.7	1018.5	5.7	1030.9	0.0
	1033.6	221.4	1057.1	148.8	1057.1	148.8
	1535.9	12.4	1535.9	12.4	1553.8	174.3
	3374.3	151.6	3374.3	151.5	3378.6	85.4
	3458.7	15.4	3459.2	48.4	3459.2	48.4
	3512.5	3.1	3512.5	3.1	3514.7	141.2

Table 3s. Total energies at 0K, total energies at 298 K (ZPVE included), in Hartree, and standard entropies ($\text{J mol}^{-1} \text{K}^{-1}$) of investigated compounds. B3LYP/pVDZ level of theory.

Compound	E_0 total, Hartree	E_{298} (ZPVE included), Hartree	S_{298}^0 , $\text{J mol}^{-1} \text{K}^{-1}$
H_2	-1.1737901	-1.161473	130.7
HCl	-460.6700685	-460.660967	186.7
N_2	-109.4392217	-109.431190	191.5
GaCl	-2384.7939364	-2384.790391	239.8
GaCl_2	-2844.8739178	-2844.867722	303.1
GaCl_3	-3305.0272375	-3305.017683	325.8
Ga_2Cl_6	-6610.0879468	-6610.066088	510.5
NH	-55.1747974	-55.165086	181.2
NH_2	-55.8309529	-55.809293	194.9
NH_3	-56.5094756	-56.472574	192.5
$\text{GaN } ^1\Sigma^+$	-1979.1844290	-1979.180159	223.3
$\text{GaN } ^3\Pi$	-1979.2314103	-1979.227510	234.7
Cl_3GaNH_3	-3361.5925311	-3361.541588	384.7
Cl_2GaNH_2	-2900.8414765	-2900.807479	344.7
$\text{ClGaNH } ^1\text{A}'$	-2440.0296269	-2440.011760	289.3
$\text{ClGaNH } ^3\text{A}''$	-2439.9994476	-2439.982712	316.3
$(\text{ClGaNH})_2$	-4880.2326376	-4880.191213	391.8
$(\text{ClGaNH})_3$	-7320.4280688	-7320.363466	503.4
$(\text{ClGaNH})_4$	-9760.6351537	-9760.547883	540.7
$(\text{ClGaNH})_6$	-14641.0141111	-14640.881014	738.4
$(\text{Cl}_2\text{GaNH}_2)_2$	-5801.7764624	-5801.703137	479.1
$(\text{Cl}_2\text{GaNH}_2)_3$	-8702.6827539	-8702.570306	656.4
$(\text{Cl}_3\text{GaNH}_3)_2$	-6723.2125655	-6723.107532	603.0
$\text{NH}_3^*\text{Cl}_2\text{GaNH}_2$	-2957.3969376	-2957.321522	397.0
$\text{Cl}_2\text{GaNH}_2^*\text{GaCl}_3$	-6205.9360975	-6205.888361	498.2
$\text{NH}_3^*\text{Cl}_2\text{GaNH}_2^*\text{GaCl}_3$	-6262.4754440	-6262.386351	575.6
$\text{Cl}_3\text{GaNH}_3^*\text{HCl}^*\text{Cl}_2\text{GaNH}_2$	-6723.1337324	-6723.034162	649.7
$\text{Cl}_9\text{Ga}_6\text{N}_6\text{H}_9$	-16023.2269351	-16023.045471	867.1

Figure 1s. Gibbs energy – temperature diagram for the gas phase reactions. Partial pressures of all gas phase species are fixed at 1 atm.

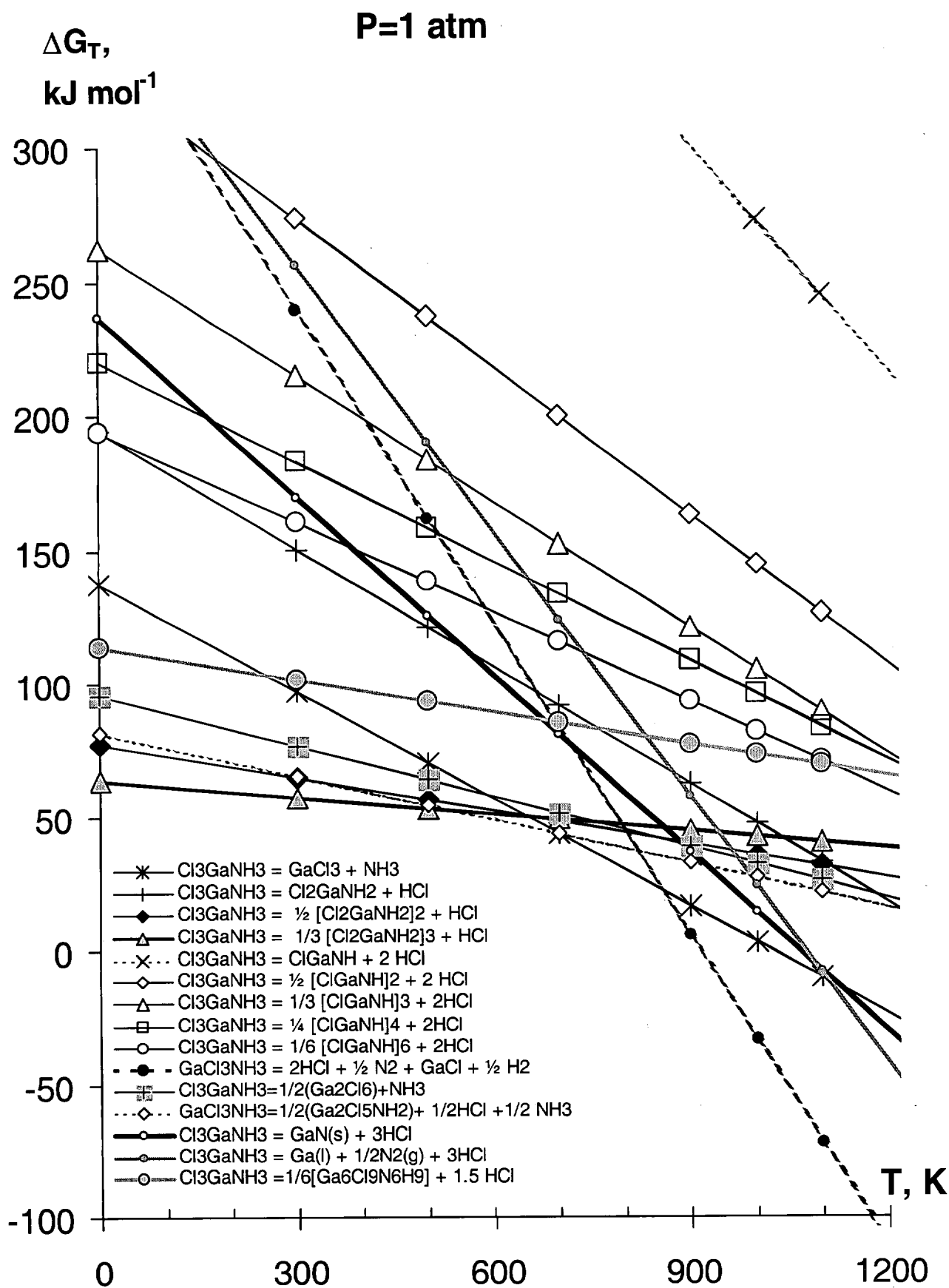


Figure 2s. Gibbs energy – temperature diagram for the gas phase reactions. Partial pressures of all gas phase species are fixed at 0.01 atm.

