Thermodynamic Functions for Nitrosyl Chloride

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LANDAU AND FLETCHER (5) have determined the vibrational fundamentals and the six anharmonicity terms. Rogers and others (7) have determined the rotational constants, and these were recently confirmed by Millen and Pannell (6). No information on vibration-rotation interaction or rotational stretching was found in the literature. Nine vibration-rotation coefficients (α_{ij}) would be expected for a nonlinear molecule. If such coefficients were available, consideration of them might increase C_p° at 6000° K. (the most sensitive function) by 3 to 4%. Determination of these coefficients is difficult—indeed, they are not available for the commonly studied gas SO_2.

Thermodynamic functions were computed by the IBM 650 EDPM using a program described previously (3). In these calculations, R is 1.98726 cal. per mole degree, hc/k is 1.4388, and the Sackur-Tetrode constant K_6 is −7.28353 (2). For nitrosyl bromide, the functions computed by Burns and Bernstein (1) were checked and found satisfactory. Data for nitrosyl fluoride have been given in another article (4).

Table I. Thermodynamic Functions for ClNO (g)

T, ° K.	$-(F^\circ - H^\circ_0)/T$	$(H^\circ - H^\circ_0)/T$	S°	C_p°, Cal. Mole^{-1} Deg.$^{-1}$	$H^\circ_T - H^\circ_{298}$, Kcal. Mole^{-1}
298.15	53.415	9.112	62.527	10.680	...
300	53.471	9.122	62.593	10.694	0.0197
400	56.163	9.596	65.759	11.311	1.1217
500	58.348	9.989	68.336	11.790	2.2776
600	60.199	10.324	70.523	12.196	3.4776
700	61.813	10.617	72.429	12.535	4.7147
800	63.248	10.875	74.123	12.827	5.9832
900	64.543	11.106	75.648	13.069	7.2781
1000	65.724	11.312	77.035	13.273	8.5953
1100	66.811	11.498	78.309	13.446	9.9313
1200	67.818	11.667	79.485	13.597	11.2835
1300	68.758	11.820	80.578	13.726	12.6496
1400	69.640	11.961	81.600	13.841	14.0279
1500	70.469	12.089	82.558	13.943	15.4170
1600	71.253	12.208	83.461	14.035	16.8158
1700	71.997	12.318	84.314	14.120	18.2235
1800	72.704	12.420	85.123	14.195	19.6391
1900	73.378	12.515	85.893	14.266	21.0623
2000	74.022	12.605	86.626	14.335	22.4923
2100	74.639	12.688	87.327	14.396	23.9288
2200	75.231	12.767	87.998	14.458	25.3715
2300	75.800	12.842	88.642	14.515	26.8201
2400	76.349	12.913	89.261	14.570	28.2742
2500	76.877	12.980	89.857	14.623	29.7338
2600	77.387	13.044	90.431	14.675	31.1985
2700	77.881	13.106	90.986	14.724	32.6682
2800	78.359	13.164	91.522	14.771	34.1429
2900	78.821	13.220	92.041	14.820	35.6223
3000	79.271	13.274	92.545	14.866	37.1064
3100	79.707	13.326	93.033	14.910	38.5951
3200	80.131	13.377	93.507	14.957	40.0882
3300	80.543	13.425	93.968	14.997	41.5858
3400	80.944	13.472	94.416	15.044	43.0877
3500	81.336	13.517	94.853	15.083	44.5939
3600	81.717	13.561	95.278	15.126	46.1044
3700	82.089	13.604	95.693	15.169	47.6190
3800	82.453	13.646	96.098	15.210	49.1378
3900	82.808	13.687	96.494	15.251	50.6607
4000	83.155	13.726	96.880	15.292	52.1877
4100	83.494	13.765	97.258	15.333	53.7188
4200	83.826	13.803	97.628	15.371	55.2539
4300	84.151	13.840	97.990	15.411	56.7930
4400	84.470	13.876	98.345	15.454	58.3360
4500	84.782	13.911	98.693	15.491	59.8830
4600	85.088	13.946	99.034	15.530	61.4340
4700	85.389	13.980	99.368	15.570	62.9888
4800	85.683	14.013	99.696	15.608	64.5476
4900	85.973	14.046	100.018	15.647	66.1102
5000	86.257	14.079	100.335	15.688	67.6768
5100	86.536	14.111	100.646	15.721	69.2472
5200	86.810	14.142	100.952	15.766	70.8214
5300	87.080	14.173	101.252	15.798	72.3995
5400	87.345	14.203	101.548	15.838	73.9814
5500	87.606	14.233	101.839	15.878	75.5671
5600	87.863	14.263	102.125	15.911	77.1566
5700	88.115	14.292	102.407	15.951	78.7500
5800	88.364	14.321	102.685	16.002	80.3470
5900	88.609	14.350	102.959	16.027	81.9480
6000	88.851	14.378	103.228	16.066	83.5527

Table II. Molecular Constants of ClNO, Cm.$^{-1}$

(Natural isotopic mixture)

Molecular Weight = 65.465

σ_1	1800.0	$-X_{11}$	18.3
σ_2	594.9	$-X_{22}$	8.0
σ_3	331.5	$-X_{33}$	2.0
A_0	2.847	$-X_{12}$	8.0
B_0	0.19028	$-X_{23}$	4.9
C_0	0.17835	$-X_{13}$	3.9

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RECEIVED for review August 7, 1961. Accepted October 11, 1961.