these compound types according to the relative crowding of the nitrogen atom, as in the classification scheme of Table XI. Similarly, nonortho alkyl substitution increases S° for these compounds much more than in the case of the aromatic hydrocarbons of similar ring number, and pure compound data (*39*) were used to estimate the additional contribution to ΔS° in excess of that given by Figure 2.

Given values of ΔA_s and of ΔS° for the effect of aliphatic substitution on the original S° and A_s values of a parent molecule, it may be shown that

$$\epsilon_1 = [(A_s/A_s + \Delta A_s)](\epsilon_1)^\circ + \Delta S^\circ/(A_s + \Delta A_s)$$

ϵ_1 refers to the value for the aliphatic substituted derivative—i.e., petroleum component—and $(\epsilon_1)^\circ$ is the value of ϵ_1 for the original parent compound.

With the exception of basic nitrogen compounds, compounds of the same type fall into reasonably narrow adsorptivity ranges, as illustrated in Figure 3.

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Thermodynamic Functions of Cyanogen Bromide

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THERMODYNAMIC DATA for BrCN are required in the analysis of combustion of high density oxygen deficient systems with various amine fuels.

As a result of recent higher resolution infrared studies, Maki and Gott (*7*) have determined the rotation-vibration interaction term, α_3, and the doubling coefficient, g_{22}. Maki (*6*) has determined the anharmonic terms, x_{22}, x_{23}, and ($\nu_1 + x_{13}$). Burrus and Gordy (*1*) determined the rotational constant, B_0 and the rotational stretch constant, D_0. Townes, Holden, and Merritt (*9*) have determined the α_2 value. Freitag and Nixon (*4*) have determined the observed fundamentals, σ_i; their older values of x_{22}, x_{23}, and g_{22} when used in a comparison calculation led to less satisfactory values of the thermodynamic functions. Maki

Table I. Thermodynamic Functions for BrCN(g)

Temp., °K.	$\frac{-(F^\circ - H^\circ_0)}{T}$	$\frac{(H^\circ - H^\circ_0)}{T}$	S°	C°_p, Cal. Mole^{-1} Deg.$^{-1}$	$H^\circ_T - H^\circ_{298}$, Kcal. Mole^{-1}	F°/RT
298.15	50.447	8.887	59.334	11.263	0.0	50.345
300	50.502	8.902	59.403	11.280	0.021	49.850
400	53.162	9.592	62.753	11.983	1.187	29.696
500	55.361	10.119	65.480	12.451	2.410	17.300
600	57.245	10.540	67.784	12.826	3.674	8.826
700	58.896	10.890	69.786	13.150	4.973	2.619
800	60.371	11.191	71.561	13.433	6.303	−2.155
900	61.704	11.454	73.158	13.680	7.659	−5.962
1000	62.923	11.688	74.611	13.895	9.038	−9.085
1100	64.047	11.897	75.944	14.081	10.437	−11.703
1200	65.091	12.086	77.176	14.244	11.853	−13.938
1300	66.065	12.257	78.322	14.386	13.285	−15.876
1400	66.979	12.414	79.393	14.511	14.730	−17.576
1500	67.840	12.558	80.398	14.621	16.187	−19.085
1600	68.655	12.690	81.345	14.720	17.654	−20.436
1700	69.428	12.812	82.240	14.809	19.130	−21.655
1800	70.164	12.925	83.089	14.890	20.615	−22.763
1900	70.865	13.030	83.896	14.965	22.108	−23.776
2000	71.536	13.129	84.665	15.033	23.608	−24.708
2100	72.179	13.221	85.400	15.096	25.115	−25.569
2200	72.796	13.308	86.104	15.155	26.627	−26.368
2300	73.390	13.389	86.779	15.211	28.145	−27.113
2400	73.961	13.466	87.427	15.263	29.669	−27.810
2500	74.512	13.539	88.051	15.313	31.198	−28.463
2600	75.045	13.608	88.653	15.361	32.732	−29.079
2700	75.560	13.674	89.234	15.406	34.270	−29.659
2800	76.058	13.737	89.795	15.450	35.813	−30.209
2900	76.541	13.796	90.338	15.492	37.360	−30.730
3000	77.010	13.854	90.863	15.533	38.911	−31.225
3100	77.465	13.909	91.373	15.573	40.467	−31.697
3200	77.907	13.961	91.868	15.612	42.026	−32.147
3300	78.338	14.012	92.349	15.650	43.589	−32.578
3400	78.757	14.060	92.817	15.687	45.156	−32.990
3500	79.165	14.107	93.272	15.723	46.726	−33.385
3600	79.563	14.153	93.716	15.758	48.301	−33.765
3700	79.951	14.197	94.148	15.793	49.878	−34.130
3800	80.331	14.239	94.570	15.828	51.459	−34.481
3900	80.701	14.280	94.981	15.861	53.044	−34.820
4000	81.063	14.320	95.383	15.895	54.631	−35.147
4100	81.417	14.359	95.776	15.928	56.223	−35.462
4200	81.764	14.397	96.160	15.961	57.817	−35.768
4300	82.103	14.434	96.536	15.993	59.415	−36.064
4400	82.435	14.469	96.904	16.025	61.016	−36.350
4500	82.761	14.504	97.265	16.057	62.620	−36.628
4600	83.080	14.538	97.618	16.088	64.277	−36.898
4700	83.393	14.572	97.964	16.119	65.837	−37.160
4800	83.700	14.604	98.304	16.150	67.451	−37.414
4900	84.001	14.636	98.637	16.181	69.067	−37.662
5000	84.297	14.667	98.965	16.212	70.687	−37.903
5100	84.588	14.698	99.286	16.242	72.310	−38.138
5200	84.874	14.728	99.602	16.273	73.935	−38.367
5300	85.155	14.757	99.912	16.303	75.564	−38.590
5400	85.431	14.786	100.217	16.333	77.196	−38.808
5500	85.702	14.815	100.517	16.363	78.831	−39.021
5600	85.970	14.843	100.812	16.392	80.468	−39.228
5700	86.232	14.870	101.102	16.422	82.109	−39.431
5800	86.491	14.897	101.388	16.452	83.753	−39.630
5900	86.746	14.924	101.670	16.481	85.400	−39.824
6000	86.997	14.950	101.947	16.510	87.049	−40.014

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

Natural Isotopic Mixture

$\sigma_1 = 575$
$\sigma_2 = 342.5$
$\sigma_3 = 2200$
$\alpha_1 = 5.17 \times 10^{-4}$
$\alpha_2 = -3.84 \times 10^{-4}$
$\alpha_3 = 6.77 \times 10^{-4}$
$B_0 = 0.13705$
$D_0 = 2.929 \times 10^{-8}$

$-x_{11} = 3.0$
$-x_{22} = 0.86$
$-x_{33} = 5.0$
$-x_{12} = 4.0$
$-x_{23} = 6.19$
$-x_{13} = 3.0$
$g_{22} = 1.14$

Molecular weight = 105.934
Heat of formation $\Delta H^\circ_{f_0} = +44.87$ kcal./mole (*3*).

and Gott (*7*) list an α_1 value which is ascribed to Tetenbaum (*8*) and is used in preference to the older value (3.77×10^{-4}) given by Townes, Holden, and Merritt (*9*).

It is necessary to estimate values for the anharmonic terms x_{11}, x_{33}, x_{12}, and x_{13} in a reasonable manner based on data for related linear molecules (ClCN, COS, CO_2, N_2O), since there appears to be considerable difficulty in obtaining accurate values for these terms from the observed BrCN spectra.

Thermodynamic functions were computed over the temperature range 298° to 6000° K., for an ideal gas of BrCN molecules at 1 atm. using the program described previously (*5*). 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*). Previous tables for BrCN were based on the rigid rotorharmonic oscillator (RRHO) approximation.

Consideration of the anharmonicities and rotational effects raises C_p° (6000° K.) 11% beyond the RRHO result.

NOMENCLATURE

α = rotation-vibration interaction coefficient, cm.$^{-1}$
B = rotational constant, cm.$^{-1}$
C_p = specific heat capacity, cal. mole^{-1} deg.$^{-1}$
D = rotational stretching coefficient, cm.$^{-1}$
ΔH_f = heat of formation, kcal. mole^{-1}
F = free energy, cal. mole^{-1}
g = doubling coefficient for degenerate vibration, cm.$^{-1}$
H = enthalpy, cal. mole^{-1}
R = gas constant, 1.98726 cal. mole^{-1} deg.$^{-1}$
σ = vibrational fundamental energy, cm.$^{-1}$
S = entropy, cal. mole^{-1} deg.$^{-1}$
T = temperature, ° K.
X = anharmonicity term, cm.$^{-1}$

Superscript

$^\circ$ = ideal gas standard state (1 atm.)

Subscript

0, 1, 2, 3 = vibrational identification

Subscript

0 = zero deg. K.

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