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GENERAL MOTORS CORPORATION

TECHNICAL REPORT

ON

APPROXIMATE THERMODYNAMIC FUNCTIONS
FOR THE $\text{CN}^+(\text{g})$ AND $\text{CN}^-(\text{g})$ IONS

Sponsored By

ADVANCED RESEARCH PROJECTS AGENCY

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HYPERVELOCITY RANGE RESEARCH PROGRAM

A PART OF PROJECT "DEFENDER"

GM DEFENSE RESEARCH LABORATORIES

SANTA BARBARA, CALIFORNIA



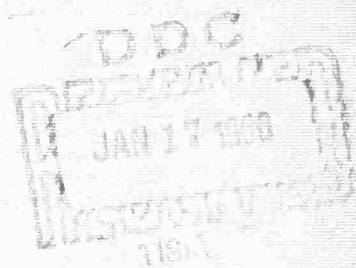
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ON
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FOR THE $\text{CN}^+(\text{g})$ AND $\text{CN}^-(\text{g})$ IONS

By
David G. Clifton

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FOREWORD

This report is one of a series of related papers covering various aspects of a broad program to investigate the flow-field variables associated with hypersonic-velocity projectiles in free flight under controlled environmental conditions. The experimental research is being conducted in the Flight Physics Range of GM Defense Research Laboratories, General Motors Corporation, and is supported by the Advanced Research Projects Agency under Contract No. DA-01-021-AMC-11359(Z). It is intended that this series of reports, when completed, will provide a background of knowledge of the phenomena involved in the basic study and thus aid in a better understanding of the data obtained in the investigation.

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ABSTRACT

Approximate values have been calculated for the free-energy and enthalpy functions and the entropy and constant-pressure heat capacity for the ions $\text{CN}^+(\text{g})$ and $\text{CN}^-(\text{g})$. A review of the available experimental data is presented with a recommendation for the values of the heats of formation of these same ions.

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I. INTRODUCTION

One common feature of most ablative materials which are used for thermal protection of reentry vehicles is that they contain the element carbon in some form.⁽¹⁻⁴⁾ When these materials ablate they interact chemically with hot air and the resulting chemistry has marked effects upon the observables of the flow fields. Particularly, ionization of some of the products and/or chemionization during some of the reactions produce electrons which affect the radar observables.

To better understand the chemistry of the mixtures of hot air and ablation materials, it is of interest to make calculations of the possible resulting compositions. These calculations require a knowledge of the thermodynamic functions of the various species which may contribute to the overall composition, and in some instances there is a lack of the necessary thermodynamic functions. Such is the case for the two ionic species CN^+ and CN^- . This report presents some approximate thermodynamic functions for these ions as well as an explanation of how these functions were obtained.

The two ionic species, CN^+ and CN^- , are normally considered to arise from the ionization of CN or from an electron attachment to CN. It has been shown in equilibrium calculations of the compositions of carbon-air systems^(5,6) that the concentrations of CN can become comparable to and/or greater than the concentrations of other ionized species under certain conditions; therefore, contributions to the electrical properties of the mixture may be made by the ionic species CN^+ and CN^- .

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Furthermore, the fact that CN molecules are present in the atmosphere of ablating models has been established by the spectroscopic observations^(7, 8, 9) of the emission of excited CN molecules in the flow fields of models flown in a free-flight range.

Still another point of interest concerning these species results from some experimental observations made by Utterback⁽¹⁰⁾ with a molecular beam apparatus. He finds evidence for the reaction $N_2 + CO \rightarrow CN^- + NO^+$ when he bombards the CO with neutral nitrogen. He also finds that an endothermicity of about 12 ev for this reaction fits his data, which is in agreement with the theoretical expectations.

In a system of hot air and ablation material containing carbon, two of the most prevalent species are N_2 and CO,⁽⁵⁾ and if it is considered that the CN^- ion would not be very stable at very high temperatures (i.e., $CN^- \rightarrow CN + e^-$) this series of reactions offers possibilities as a source of electrons.

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II. THE $\text{CN}^+(\text{g})$ ION

Experimental spectroscopic data for the CN^+ ion has been reported by Douglas and Routley.^(11, 12) These workers observed two emission band systems of CN^+ which they analyzed as $^1\Sigma - ^1\Sigma$ transitions.* They also observed four bands as yet unidentified. From their analysis they present the constants shown below in Table I, and have tentatively assigned the a $^1\Sigma$ state as the ground state.

Table I
(from Reference 12)
CONSTANTS OF THE THREE $^1\Sigma$ STATES IN $\text{CN}^+(\text{g})$

State	T_e (cm^{-1})	ω_e (cm^{-1})	$\omega_e x_e$ (cm^{-1})	B_0 (cm^{-1})	D_0 (cm^{-1})	B_e (cm^{-1})	α_e (cm^{-1})	r_e (10^{-8}cm)
a $^1\Sigma$	0	2033.05	16.14	1.8871	7.0×10^{-6}	1.8964	0.0186	1.1727
c $^1\Sigma$	31,771	1285	11	1.402	13×10^{-6}	1.463	0.002	1.363
f $^1\Sigma$	45,533.6	2610.5	46.9	1.8870	4.7×10^{-6}	1.903	0.032	1.171

An estimation can be made of the temperature at which the first excited electronic state will contribute appreciably to the thermodynamic functions. Using the rough rule that if any level, E/k , is greater than $5T$ then its contribution can be neglected, it can be seen that the first excited level will not contribute appreciably below about $9,000^\circ\text{K}$. ($E = \nu hc$ where ν is in cm^{-1} , h = Planck constant, c = velocity of light, k = Boltzman constant, and $T = ^\circ\text{K}$.)

* The spectroscopic symbolism used here and subsequently is consistent with that given in Reference 25.

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The free energy function, $-(F^0 - H_0^0)/T$, enthalpy function, $(H^0 - H_0^0)/T$, entropy, S^0 , and heat capacity at constant pressure, C_p , for CN^+ over the temperature range from 298°K to 5,000°K are given in Table II. These thermodynamic functions have been calculated from the usual statistical thermodynamic expressions⁽¹³⁾ for a rigid-rotator, harmonic-oscillator molecule with the rotational partition function taking the classical value. The spectroscopic constants used were $B_0 = 1.8871 \text{ cm}^{-1}$ and $\omega_0 = 2016.91 \text{ cm}^{-1}$ as obtained from Table I. The ground electronic state is a singlet. The molecular weight is taken as 26.019, the symmetry number, σ , is equal to 1, $R = 1.98717 \text{ cal/mole } ^\circ\text{K}$, and the values for the other fundamental constants were taken from those recently adopted by the National Bureau of Standards.⁽¹⁴⁾

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Table II
THERMODYNAMIC FUNCTIONS FOR $\text{CN}^+(\text{g})$

T (°K)	$-(F^\circ - H^\circ_0)/T$	$(H^\circ - H^\circ_0)/T$	S°	C_F
(cal/deg-mole)				
298.15	40.072	6.956	47.028	6.966
300	40.115	6.956	47.071	6.967
400	42.117	6.965	49.082	7.029
600	44.952	7.032	51.983	7.330
800	46.990	7.152	54.142	7.689
1000	48.601	7.290	55.891	7.985
1200	49.942	7.425	57.367	8.203
1400	51.096	7.548	58.644	8.362
1600	52.111	7.657	59.768	8.477
1800	53.019	7.753	60.772	8.563
2000	53.340	7.838	61.678	8.628
2200	54.591	7.912	62.502	8.678
2400	55.282	7.977	63.259	8.718
2600	55.923	8.035	63.958	8.749
2800	56.520	8.087	64.607	8.775
3000	57.080	8.134	65.214	8.795
3200	57.606	8.176	65.782	8.812
3400	58.103	8.213	66.316	8.827
3600	58.573	8.248	66.821	8.839
3800	59.020	8.279	67.299	8.849
4000	59.440	8.308	67.753	8.858
4200	59.852	8.334	68.186	8.866
4400	60.240	8.358	68.598	8.873
4600	60.612	8.381	68.993	8.879
4800	60.969	8.402	69.371	8.884
5000	61.312	8.421	69.733	8.888
5200	61.643	8.439	70.082	8.892
5400	61.962	8.456	70.418	8.896
5600	62.270	8.472	70.741	8.899
5800	62.567	8.486	71.054	8.902
6000	62.855	8.500	71.355	8.905

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The other thermodynamic quantity which is necessary in equilibrium calculations is the standard heat of formation, ΔH_O^0 . For the CN^+ ion this would be equal to the sum of the heat of formation of CN and the ionization potential of CN.

The heat of formation of CN is controversial; however, a rather extensive discussion of the various values and experiments is presented in the JANAF Tables ⁽¹⁵⁾ and this evaluation, which appears very reasonable, is that ΔH_O^0 for CN is 108.215 kcal/mole or 4.69 ev. This is the value which will be used here.

A number of different values have been reported for the ionization energy of CN. Berkowitz ⁽¹⁶⁾ reports the only direct measurement of the ionization of CN radicals by electron impact as 14.2 ± 0.3 ev; yet in some experiments at high intensity he saw a "tail" down to lower voltages which he attributes to contamination by C_2H_2^+ . In this same paper the appearance potential of CN^+ from C_2N_2 was given as 20.4 ± 0.3 ev, where the CN^+ was considered to have excess kinetic energy of 0.57 ev. The recommended value of $D(\text{NC-CN})$ in this paper is 6.2 ev (which corresponds to the JANAF value). Combining these latter values one obtains:

$$\text{AP}(\text{CN}^+) = D(\text{NC-CN}) + I(\text{CN}) + .57 \text{ ev}$$

or

$$I(\text{CN}) = 20.4 - 6.2 - .6 = 13.6 \text{ ev}$$

So within this paper there are two values for the ionization energy of CN.

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Herron and Dibeler⁽¹⁷⁾ present studies of electron impact measurements on cyanogen halides. They interpreted their data in terms similar to Stevenson⁽¹⁸⁾ where the CN fragments were considered to be in an excited state. Knight and Riese⁽¹⁹⁾ discuss how these data can be reinterpreted in such a manner as to lead to the accepted JANAF value for the heat of formation of CN.

The appearance-potential measurements made by Herron and Dibeler⁽¹⁷⁾ can be combined by a method of taking differences (which should cancel any systematic errors in the absolute determinations of their values) such that the ionization potential of CN is given. Those authors made the following measurements:

(1)	$\text{CnCl} \rightarrow \text{CN} + \text{Cl}^+ + \bar{e}$	$(\text{AP})_1 = 17.9 \text{ ev}$
(2)	$\text{CnCl} \rightarrow \text{CN}^+ + \text{Cl} + \bar{e}$	$(\text{AP})_2 = 18.3 \text{ ev}$
(3)	$\text{CNBr} \rightarrow \text{CN} + \text{Br}^+ + \bar{e}$	$(\text{AP})_3 = 16.2 \text{ ev}$
(4)	$\text{CNBr} \rightarrow \text{CN}^+ + \text{Br} + \bar{e}$	$(\text{AP})_4 = 18.3 \text{ ev}$
(5)	$\text{CnI} \rightarrow \text{CN} + \text{I}^+ + \bar{e}$	$(\text{AP})_5 = 14.3 \text{ ev}$
(6)	$\text{CnI} \rightarrow \text{CN}^+ + \text{I} + \bar{e}$	$(\text{AP})_6 = 18.1 \text{ ev}$

The energies are such that process (2) minus process (1) gives:

$$\Delta H_f(\text{CN}^+) - \Delta H_f(\text{CN}) = (\text{AP})_2 - (\text{AP})_1 + \Delta H_f(\text{Cl}^+) - \Delta H_f(\text{Cl})$$

$$I(\text{CN} - \text{CN}^+) = (\text{AP})_2 - (\text{AP})_1 + I(\text{Cl} - \text{Cl}^+)$$

$$I(\text{CN}) = 18.3 - 17.9 + 13.01 = 13.41 \text{ ev}$$

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Similar to (3) and (4) and (5) and (6) may be coupled to give $I(\text{CN}) = 13.94 \text{ ev}$ and 14.24 ev , respectively.

Employing a similar approach of taking differences of the appearance potentials for the reactions studied by Stevenson⁽¹⁸⁾ (neglecting the idea of the CN being in an excited electronic level) his data yields ionization potentials for CN. The reactions and appearance potentials given in this paper are:



From processes (7) and (8) we get:

$$(\text{AP})_7 - (\text{AP})_8 = \Delta H_f(\text{CN}^+) - \Delta H_f(\text{CN}) + \Delta H_f(\text{H}) - \Delta H_f(\text{HCN}) - \Delta H_f(\text{Cl}^+) + \Delta H_f(\text{ClCN})$$

$$\text{or } I(\text{CN} \rightarrow \text{CN}^+) = 1.55 \text{ ev} - \Delta H_f(\text{H}) + \Delta H_f(\text{HCN}) + \Delta H_f(\text{Cl}^+) - \Delta H_f(\text{ClCN})$$

where	$\Delta H_f(\text{H}) = 2.24 \text{ ev}$	(from Reference 20)
	$\Delta H_f(\text{HCN}) = 1.35 \text{ ev}$	(from Reference 21)
	$\Delta H_f(\text{Cl}^+) = 14.3 \text{ ev}$	(from Reference 22)
	$\Delta H_f(\text{ClCN}) = 1.37 \text{ ev}$	(from Reference 23)
	$\Delta H_f(\text{CN})_2 = 3.18 \text{ ev}$	(from Reference 15)

Therefore,

$$I(\text{CN} \rightarrow \text{CN}^+) = 13.6 \text{ ev}$$

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Similarly, from processes (8) and (9),

$$(AP)_9 - 2(AP)_8 = \Delta H_f(CN^+) - \Delta H_f(CN) - 2\Delta H_f(CI^+) + 2\Delta H_f(CICN) - \Delta H_f(CN)_2$$

$$\text{or } I(CN \rightarrow CN^+) = -15.31 + 28.6 - 2.74 + 3.18$$

$$I(CN \rightarrow CN^+) = 13.7 \text{ ev}$$

Also, if one uses the data of the paper of Kandel⁽²⁴⁾ coupled with the JANAF value for the dissociation of C_2N_2 , one gets:

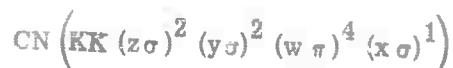
$$I(CN \rightarrow CN^+) = 13.9 \text{ ev}$$

To summarize these results we see that they give ionization potential values of 14.2, 13.6, 13.4, 13.9, 14.2, 13.6, 13.7, and 13.9 ev. Since all of these were determined by electron impact methods, and in this method the results may include kinetic energies of the particles, it is considered best to use the lower values. Therefore, the value of 13.4 ev will be used here as a value consistent with the choice of the heats formation of CN and C_2N_2 as recommended in the JANAF compilation. Therefore, the heat of formation of CN^+ becomes:

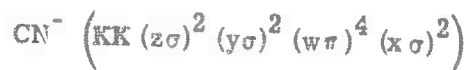
$$\Delta H_f(CN^+) = 18.1 \text{ ev} = 417,000 \text{ cal/mole.}$$

III. THE CN^- (g) ION

The electronic configuration of the ground state of the CN radical can be written in molecular orbital terminology as:



and this is confirmed by the spectroscopic observation that the ground state is $^2\Sigma^+$ (See Reference 25). Since the CN^- ion is formed by the addition of an electron, it is reasonable to assume that its electronic configuration should be given as:



and would therefore have a $^1\Sigma^+$ ground state. Because this added electron is going into a bonding orbital the CN^- ion should be relatively stable, and indeed observations of its existence have been made using mass spectrometers. (26-29)

Although the additional bonding orbital confirms some stability on the ion and it might be expected to thereby have an interatomic distance shortened over that of the CN radical, the overall negative charge on the ion would have the tendency to lengthen the bond due to mutual repulsion of the orbiting electrons. It is therefore reasonable, as a first approximation, to assume that these two effects cancel one another so that the CN^- ion would have about the same internuclear distance as the CN radical; consequently, the assumption that the ion has the same rotational constant and vibrational frequency as the CN radical is a good approximation.

Since CN^- is isoelectronic with the N_2 and CO molecules the first excited singlet electronic state would be expected to lie about 8 eV above the ground state. This energy is greater than the anticipated electron affinity (EA) of the CN radical so these excited electronic states are not expected to contribute to the thermodynamic functions of the CN^- ion.

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By following the same calculational procedures discussed above for the CN^+ ion, the thermodynamic functions have been calculated and are given in Table III. The spectroscopic constants which have been used were deduced from the tabulated data by Herzberg⁽²⁵⁾ for the CN radical and are:

$$B_0 = 1.8909 \quad \sigma = 1$$

$$\omega_0 = 2055.57 \quad g = 1$$

The above cited universal constants were used and the molecular weight was taken to be 26.000, in agreement with the Herzberg data.

Table III
THERMODYNAMIC FUNCTIONS FOR $\text{CN}^-(g)$

T (°K)	$-(F^0 - H_0^0)/T$	$(H^0 - H_0^0)/T$	S^0	C_p
	(cal/deg-mole)			
298.15	40.066	6.956	47.022	6.965
300	40.109	6.956	47.065	6.965
400	42.111	6.964	49.075	7.022
600	44.944	7.026	51.970	7.310
800	46.980	7.142	54.122	7.664
1000	48.588	7.277	55.865	7.960
1200	49.927	7.410	57.337	8.182
1400	51.079	7.533	58.611	8.344
1600	52.092	7.642	59.733	8.462
1800	52.998	7.738	60.735	8.550
2000	53.817	7.823	61.640	8.617
2200	54.566	7.897	62.464	8.669
2400	55.254	7.963	63.220	8.710
2600	55.896	8.022	63.918	8.742
2800	56.493	8.074	64.567	8.768
3000	57.051	8.121	65.172	8.790
3200	57.577	8.163	65.740	8.808
3400	58.073	8.202	66.275	8.823
3600	58.543	8.237	66.779	8.835
3800	58.989	8.268	67.257	8.846
4000	59.414	8.297	67.711	8.855
4200	59.819	8.324	68.143	8.863
4400	60.207	8.349	68.556	8.870
4600	60.579	8.371	68.950	8.876
4800	60.935	8.393	69.328	8.882
5000	61.278	8.412	69.691	8.886
5200	61.609	8.430	70.039	8.891
5400	61.927	8.448	70.375	8.894
5600	62.235	8.463	70.698	8.898
5800	62.532	8.478	71.010	8.901
6000	62.820	8.493	71.312	8.904

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In order to arrive at a heat of formation, ΔH_0^0 , for the CN^- ion and to preserve a consistency among the data for CN , CN^+ , and CN^- , it is necessary to examine the reported experimental data.

The heat of formation of the CN^- ion is equal to the sum of the heat of formation of CN plus the electron affinity, $\text{EA}(\text{CN})$, of the CN radical.

The heat of formation of CN is taken to be that of the JANAF Tables, equal to 108.215 kcal/mole or 4.69 ev, and this is consistent with the heat of formation for C_2N_2 , as reported by JANAF, of 73.428 kcal/mole or 3.18 ev. These two values therefore lead to a dissociation energy of C_2N_2 into two CN 's of 143.0 kcal/mole or 6.2 ev. These quantities are given here as they are needed in the reduction of the reported data for the electron affinity of CN .

A recent determination of the electron affinity of CN has been made by Herron and Dibeler,⁽²⁸⁾ however, their final reported value is based upon the absolute values of their appearance-potential measurements combined with a heat of formation for the CN radical of 89 kcal/mole or 3.86 ev. In order to keep consistency in the thermal values for the various CN species, these results should be corrected.

The authors above made their measurements for the following processes of electron impacts:

(1)	$\text{CNCl} \rightarrow \text{CN}^- + \text{Cl}^+$	13.6 ev
(2)	$\text{CNCl} \rightarrow \text{CN} + \text{Cl}^+$	17.9 ev
(3)	$\text{CNBr} \rightarrow \text{CN}^- + \text{Br}^+$	11.9 ev
(4)	$\text{CNBr} \rightarrow \text{CN} + \text{Br}^+$	16.2 ev
(5)	$\text{CNI} \rightarrow \text{CN}^- + \text{I}^+$	9.8 ev
(6)	$\text{CNI} \rightarrow \text{CN} + \text{I}^+$	14.3 ev

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and then using their absolute values made the following type of computation:



$$\text{AP}(\text{CN}^-) = \text{AP}(\text{X}^+) = \Delta H_f(\text{CN}^-) + \Delta H_f(\text{X}^+) - \Delta H_f(\text{CNX})$$

which gives

$$\Delta H_f(\text{CN}^-) = \text{AP}(\text{CN}^-) - \Delta H_f(\text{X}^+) + \Delta H_f(\text{CNX})$$

and then they combined the average value of $\Delta H_f(\text{CN}^-)$ obtained from the three processes (1), (3), and (5) with the heat of formation of CN to get the electron affinity of CN. Making use of this same scheme, but this time utilizing the more acceptable value of 4.69 ev for the heat of formation of CN gives:

$$\text{EA}(\text{CN}) = -4.04 \text{ ev.}$$

These authors also took difference values for the pairs of processes (1) and (2), (3) and (4), and (5) and (6), which are seen to give the electron affinity of CN directly; however, they assumed the CN produced in the process to be in the first electronically excited state, i. e., $A^2\Pi$ state, and thereby corrected their results.

If these pairs of processes are used and it is assumed that the CN is in the ground state, the results become:

Processes (1) and (2) give $\text{EA}(\text{CN}) = -4.3 \text{ ev}$

Processes (3) and (4) give $\text{EA}(\text{CN}) = -4.3 \text{ ev}$

Processes (5) and (6) give $\text{EA}(\text{CN}) = -4.5 \text{ ev}$

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Previously to the above work, Pritchard⁽³⁰⁾ presented an excellent article reviewing electron affinities. A new evaluation of his presentation for the CN^- ion in terms of the heat of formation for CN of 4.69 ev must now be made.

If the data used by Sherman⁽³¹⁾ to obtain the electron affinity for CN^- from lattice energy calculations for NaCN and KCN are combined with the heat of dissociation for C_2N_2 of 6.2 ev (the value consistent with JANAF) rather than the value originally used by him, which was $D(\text{C}_2\text{N}_2) = 3.80$ ev, the data yield

from NaCN	$\text{EA}(\text{CN}) = -4.4$ ev
from KCN	$\text{EA}(\text{CN}) = -4.3$ ev.

Lederle's⁽³²⁾ crude spectroscopic extrapolation estimate for $\text{EA}(\text{CN})$ gave -4.0 ev and was not dependent upon the heats of formation of CN or C_2N_2 so need no correction.

Frank's⁽³³⁾ correction to Knipping's⁽³⁴⁾ electron impact data gives the heat of formation of CN^- to be .22 ev, which results in an $\text{EA}(\text{CN}) = -4.5$ ev.

Yatsimirskii⁽³⁵⁾ obtained a heat of formation for CN^- of .71 ev according to Pritchard and this would then give $\text{EA}(\text{CN}) = -4.0$ ev.

Pritchard then concludes that a fair analysis of the data gives for the heat of formation of CN^- a value of .43 ev $\pm$.22 ev. Combining this with the JANAF heat of formation for CN of 4.69 ev results in a new recommended value of $\text{EA}(\text{CN}) = -4.3$ ev.

It is therefore seen that using the consistent sets of heats of formation as recommended in the JANAF tables requires a value for the electron affinity

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of CN of about -4.3 ev or a little less. This value fits nicely with most of the reported data and will therefore be the value used here.

Combination of this electron affinity of -4.3 ev with the heat of formation of 4.69 ev for CN results in the following value for the heat of formation for CN^- :

$$\Delta H_0^0(\text{CN}^-) = .39 \text{ ev} \approx 9,000 \text{ cal/mole.}$$

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IV. CONCLUSIONS

Values for the free-energy and enthalpy functions, the entropy, and constant-pressure heat capacity have been computed for the CN^+ and CN^- ions.

Recommended values for the heats of formation for the CN^+ and CN^- ions of 417,000 cal/mole and 9,000 cal/mole, respectively, have been obtained from reported experimental work. These values are consistent with the heats of formation for CN and C_2N_2 recommended by the JANAF Thermochemical Panel.

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(Descriptors) Thermodynamics, Carbon, Nitrogen, Atmosphere entry, Enthalpy, Entropy, Chemical reactions, Air, Ablation, Materials, Ions, Ionization, Electrons, Wake

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