Fundamental Vibrational Frequencies and Thermodynamic Functions for Vinylacetylene, Revised Thermodynamic Functions for Hydrogen Cyanide, and Thermodynamics of Two Reactions Involved in the Synthesis of Acrylonitrile

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is practically equal to μ, compared with that which can be derived from the Busch[1] measured spontaneous polarization, namely, 1.25×10^{-18}, is to be interpreted as due to that not all the domains are parallel to the field in his experiment, or otherwise, as due to the experimental errors.

A detailed account will be published in Journal of the Physical Society of Japan or in Progress of Theoretical Physics.

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THE Raman[1,2] and infra-red[3] spectra of vinylacetylene (Fig. 1) have been reported in the literature, but no consistent assignment of the vibrational frequencies has been given. Using the recently published assignment for a
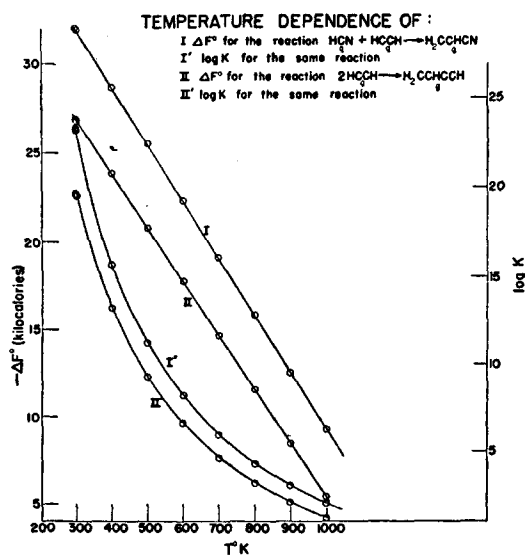

TEMPERATURE DEPENDENCE OF:

I ΔF° for the reaction $HCN + HCCH \longrightarrow H_2CCHCN$
I' log K for the same reaction
II ΔF° for the reaction $2HCCH \longrightarrow H_2CCHCCH$
II' log K for the same reaction

FIG. 1.

TABLE I. Fundamental vibration frequencies for vinylacetylene.

Description		Frequency
	Planar	
ν_1	$\equiv C-H$ stretch	3305*
ν_2		3102*
ν_3	$=C-H$ stretch	(3080)***
ν_4		3012*
ν_5	$C\equiv C$ stretch	2099*
ν_6	$C=C$ stretch	1600**
ν_7	$=CH_2$ deformation	1410**
ν_8	$=\overset{H}{\underset{\vert}{C}}-$ rock	1288*
ν_9	$=CH_2$ rock	1090**
ν_{12}	$C-C$ stretch	875*
ν_{14a}	$C\equiv C-H$ bend	615**
ν_{15}	$C=C-C$ bend	535**
ν_{17}	$C-C\equiv C$ bend	219*
	Non-planar	
ν_{10}	$C=\overset{H}{\underset{\vert}{C}}-C$ wag	950**
ν_{13}	$C=C$ torsion	678*
ν_{11}	$C=CH_2$ wag	935**
ν_{14b}	$C\equiv C-H$ bend	615**
ν_{16}	$C-C\equiv C$ bend	309*

* Reference 1.
** Reference 3.
*** Estimated.

structurally similar molecule, acrylonitrile,[4] as a basis, a reasonable choice for the fundamental vibrational frequencies of vinylacetylene can be made. This choice of frequencies, together with an approximate description of the vibrational modes, is given in Table I. The planar and non-planar bending vibrations of the $C\equiv C-H$ group have been assumed degenerate, with the frequency 615 cm^{-1}.

Using these frequencies and assuming the structural parameters given in Fig. 1, the thermodynamic functions calculated by the rigid rotator[5]-harmonic oscillator[6] approximation for vinylacetylene in the ideal gas state under one atmosphere pressure are given in Table II.

Values of the functions $(H^\circ - H_0^\circ)/T$, $(F^\circ - H_0^\circ)/T$, and S° for HCN calculated by the rigid rotator[5]-harmonic oscillator[6] approximation, and by making corrections for anharmonicity, interactions, stretching, and integration error according to the method of Wagman et al.,[7] are given in Table III. Spectroscopic values given by Herzberg[8] were used ($\nu_1 = 2089.0$, $\nu_2 = 712.1$, $\nu_3 = 3312.0$ cm^{-1}; $d_1 = 1$, $d_2 = 2$, $d_3 = 1$; $\alpha_1 = 9.3 \times 10^{-3}$, $\alpha_2 = -7 \times 10^{-4}$, $\alpha_3 = 10.8 \times 10^3$; $B_{(0)} = 1.4784$ cm^{-1}, $D = +3.3 \times 10^{-6}$, $X_{11} = -52.0$, $X_{12} = 4.2$, $X_{13} = 14.4$, $X_{22} = 2.85$, $X_{23} = 19.53$, $X_{33} = 55.48$). A com-

TABLE II. Thermodynamic functions for vinylacetylene (cal./mole/deg.).

Absolute temperature	C_p°	$H^\circ - H_0^\circ/T$	$-(F^\circ - H_0^\circ)/T$	S°
298.16	17.49	11.67	55.11	66.77
300	17.57	11.70	55.18	66.88
400	21.26	13.65	58.82	72.47
500	24.25	15.48	62.06	77.54
600	26.67	17.09	65.03	82.12
700	28.68	18.67	67.79	86.46
800	30.40	20.02	70.37	90.38
900	31.87	21.16	72.82	93.97
1000	33.16	22.39	75.10	97.48
1500	37.52	26.78	85.07	111.85

TABLE III. Values of thermodynamic functions for HCN in the ideal gaseous state (calories/deg./mole).*

$T°K$	$C_p°$	$(H°-H_0°)/T$			$-(F°-H_0°)/T$			$S°$		
	I*	I	II*	III*	I	II	III	I	II	III
298.16	8.58	7.41	7.408	7.410	40.80	40.811	40.763	48.22	48.219	48.173
300	8.59	7.42	7.416	7.413	40.85	40.856	40.810	48.27	48.272	48.223
400	9.38	7.82	7.817₅	7.812	43.04	43.046	42.997	50.85	50.863	50.809
500	9.98	8.19	8.199	8.191	44.82	44.832	44.781	53.02	53.031	52.972
600	10.47	8.53	8.544	8.534	46.35	46.356	46.305	54.88	54.900	54.839
700	10.91	8.84	8.859	8.848	47.69	47.697	47.646	56.53	56.556	56.494
800	11.30	9.12	9.149	9.134	48.89	48.898	48.845	58.01	58.046	57.979
900	11.65	9.39	9.418₅	9.401	49.98	49.989₅	49.936	59.36	59.408	59.337
1000	11.97	9.63	9.670	9.649	50.98	50.993	50.941	60.60	60.663	60.590

* The values in columns designated by I were calculated by the harmonic oscillator-rigid rotator approximation. The values in columns designated by II were calculated by the harmonic oscillator-rigid rotator approximation but were corrected in the manner discussed in the text. The values in columns designated by III are the values originally calculated by Gordon from older spectroscopic data and have been corrected here to take account of the latest values of the physical constants.

parison of these thermodynamic values with those calculated by Gordon[9] using his method[10] and slightly different spectroscopic data are also included in Table III. (Gordon's values have been corrected by the writers for changes in the best values of the fundamental and derived constants.[5])

Using these functions and relevant data from the literature, free energy changes and equilibrium constants have been calculated for two of the possible reactions in mixtures of acetylene and hydrogen cyanide.

I. $HCN(g)+HCCH(g)=H_2CCHCN(g)$. Data obtained in these laboratories[11] on the heats of combustion ($\Delta H_{298}(1$ atmos.$) = -420.82$ kcal.) and vaporization ($\Delta H_{298} = +7.850 \pm 0.050$ kcal.) of acrylonitrile, combined with the standard[5] heats of combustion for C (graphite) and $H_2(g)$, yield $+44.040$ kcal. as the heat of formation for $H_2CCHCN(g)$ at 25°C. Heats of formation for $HCN(g)$ and $HCCH(g)$ at 25°C are taken to be $+31.00$ kcal.[9] and $+54.194 \pm 0.190$ kcal.[7], respectively. Using these values we obtain

$$HCN(g)+HCCH(g)=H_2CCHCN(g);$$
$$\Delta H_{298} = -41.154 \text{ kcal./mole.}$$

From the values of $(H°-H_0°/T)$ for these substances[4,7]

$$\Delta(H°-H_0°)_{298.16} = -1.383 \text{ kcal.} = \Delta H° - \Delta H_0°.$$

Lacking data necessary to correct for gas imperfections we set $\Delta H_{298} = \Delta H°_{298.16}$, thus getting $\Delta H_0° = -39.771$ kcal./mole as the difference in zero-point energies. This constant is employed with the values of $(F°-H_0°/T)$ for the three substances[4,7] to obtain the values of $\Delta F°$ and $\log K_p$ given in Table IV and Fig. 2 for various temperatures.

TABLE IV. Free energy changes and equilibrium constants for the reactions: I. $HCN(g)+HCCH(g)=H_2CCHCN(g)$; II. $2HCCH(g) =H_2CCHCCH(g)$.

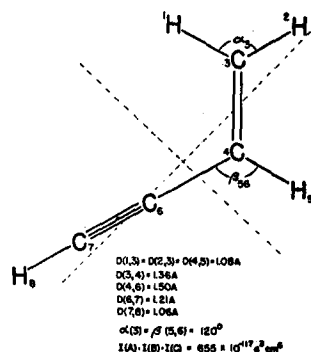| $T°K$	$\Delta F°$		$\log K_p$	
	I	II	I'	II'
298.16	-31,986	-26,900	23.4453	19.72
300	-31,932	-26,900	23.2624	19.59
400	-28,799	-23,900	15.7349	13.06
500	-25,586	-20,800	11.1835	9.09
600	-22,335	-17,800	8.1354	6.48
700	-19,065	-14,700	5.9523	4.59
800	-15,779	-11,600	4.3161	3.17
900	-12,519	-8,500	3.0400	2.06
1000	-9,261	-5,400	2.0240	1.18

FIG. 2. Structural parameters for vinylacetylene.

II. $2HCCH(g)=H_2CCHCCH(g)$. The writers could find no experimental heat of combustion value for vinylacetylene. However, calculation of ΔH_{291} for reaction I using Pauling's[12] table of bond energies yields a value only 0.05 kcal. less than the experimental one. Because of the structural similarity of the compounds involved, it is assumed that the value $\Delta H_{291} = -35.6$ kcal./mole calculated for reaction II using bond energies[12] is good to ± 0.5 kcal. Combination of this ΔH with the values of $(H_0-H_0°/T)_{291°}$ yields $\Delta H_0° = -34.3$ kcal./mole for reaction II. The values of $\Delta F°$ and $\log K_p$ calculated for reaction II using this $\Delta H_0°$ are given in Table IV and Fig. 2.

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On Rotation in Ammonium Halides

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ALTHOUGH thermodynamic evidence[1] has been obtained which is opposed to the notion that the phase transition in NH_4Cl is due to the onset of free rotation of the NH_4^+ ions, Beck's grating studies[2] of the 1750-cm⁻¹ bands in the infra-red spectra of NH_4Cl and NH_4Br showed fine structure in both room and low temperature phases which he interpreted as evidence of rotation.

We have studied the spectrum of both salts and of ND_4Cl in the temperature range, 28°C to $-190°C$, and find no evidence of rotational structure in any of the salts in either phase. The 1750-cm⁻¹ band obtained with NH_4Cl is shown in Fig. 1. The spectra of the other salts are similar.