

## On Rotation in Ammonium Halides

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Citation: *The Journal of Chemical Physics* **17**, 105 (1949); doi: 10.1063/1.1747041

View online: <http://dx.doi.org/10.1063/1.1747041>

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

T°K	C <sub>p</sub> °	(H°-H <sub>0</sub> °)/T			-(F°-H <sub>0</sub> °)/T			S°		
		I*	I	II*	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	7.817 <sub>6</sub>	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	9.418 <sub>5</sub>	9.401	49.98	49.989 <sub>5</sub>	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<sup>9</sup> using his method<sup>10</sup> 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.)

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.  $\text{HCN}(g) + \text{HCCH}(g) = \text{H}_2\text{CCHCN}(g)$ . Data obtained in these laboratories<sup>11</sup> on the heats of combustion ( $\Delta H_{298}(1 \text{ atm.}) = -420.82 \text{ kcal.}$ ) and vaporization ( $\Delta H_{298} = +7.850 \pm 0.050 \text{ kcal.}$ ) of acrylonitrile, combined with the standard<sup>5</sup> heats of combustion for C (graphite) and  $\text{H}_2(g)$ , yield  $+44.040 \text{ kcal.}$  as the heat of formation for  $\text{H}_2\text{CCHCN}(g)$  at  $25^\circ\text{C}$ . Heats of formation for  $\text{HCN}(g)$  and  $\text{HCCH}(g)$  at  $25^\circ\text{C}$  are taken to be  $+31.00 \text{ kcal.}^9$  and  $+54.194 \pm 0.190 \text{ kcal.}^7$ , respectively. Using these values we obtain  $\text{HCN}(g) + \text{HCCH}(g) = \text{H}_2\text{CCHCN}(g)$ ;

$$\Delta H_{298} = -41.154 \text{ kcal./mole.}$$

From the values of  $(H^\circ - H_0^\circ)/T$  for these substances<sup>4,7</sup>

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

Lacking data necessary to correct for gas imperfections we set  $\Delta H_{298} = \Delta H^\circ_{298.16}$ , thus getting  $\Delta H_0^\circ = -39.771 \text{ kcal./mole}$  as the difference in zero-point energies. This constant is employed with the values of  $(F^\circ - H_0^\circ)/T$  for the three substances<sup>4,7</sup> to obtain the values of  $\Delta F^\circ$  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.  $\text{HCN}(g) + \text{HCCH}(g) = \text{H}_2\text{CCHCN}(g)$ ; II.  $2\text{HCCH}(g) = \text{H}_2\text{CCHCCH}(g)$ .

T°K	$\Delta F^\circ$		$\log K_p$	
	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

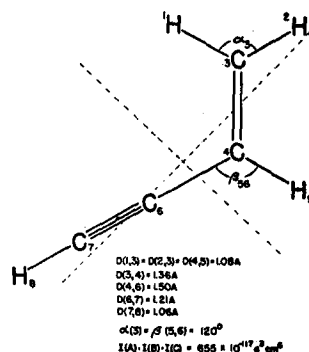


FIG. 2. Structural parameters for vinylacetylene.

II.  $2\text{HCCH}(g) = \text{H}_2\text{CCHCCH}(g)$ . The writers could find no experimental heat of combustion value for vinylacetylene. However, calculation of  $\Delta H_{291}$  for reaction I using Pauling's<sup>12</sup> 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  $\Delta H_{291} = -35.6 \text{ kcal./mole}$  calculated for reaction II using bond energies<sup>12</sup> is good to  $\pm 0.5 \text{ kcal.}$  Combination of this  $\Delta H$  with the values of  $(H_0 - H_0^\circ)/T_{291}^\circ$  yields  $\Delta H_0^\circ = -34.3 \text{ kcal./mole}$  for reaction II. The values of  $\Delta F^\circ$  and  $\log K_p$  calculated for reaction II using this  $\Delta H_0^\circ$  are given in Table IV and Fig. 2.

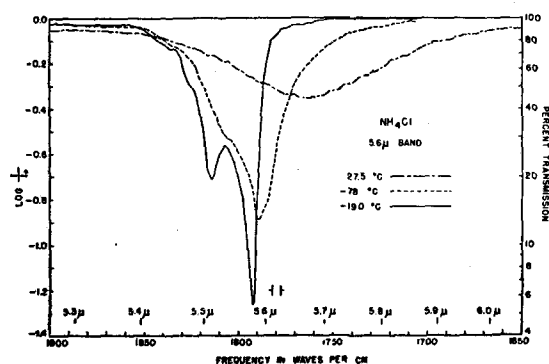
- <sup>1</sup> G. Glockler and H. M. Davis, *J. Chem. Phys.* **2**, 881 (1934).
- <sup>2</sup> P. Ganswein and R. Mecke, *Zeits. f. Physik* **99**, 189 (1936).
- <sup>3</sup> E. Bartholomé and J. Karweil, *Zeits. f. physik. Chemie* **B35**, 442 (1937).
- <sup>4</sup> F. Halverson, R. F. Stamm, and J. J. Whalen, *J. Chem. Phys.* **16**, 808 (1948).
- <sup>5</sup> Working equations given by Wagman *et al.*, *J. Research Nat. Bur. Stand.* **34**, 143 (1945) were used for the translational and rotational contributions.
- <sup>6</sup> Tables given by J. G. Aston in Taylor and Glasstone, *Treatise on Physical Chemistry* (D. Van Nostrand Company, Inc., New York, 1942), Vol. I, p. 655, were used.
- <sup>7</sup> D. D. Wagman *et al.*, *J. Research Nat. Bur. Stand.* **35**, 467 (1945).
- <sup>8</sup> G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1945), p. 280.
- <sup>9</sup> A. R. Gordon, *J. Chem. Phys.* **5**, 30 (1937).
- <sup>10</sup> A. R. Gordon, *J. Chem. Phys.* **3**, 259 (1935).
- <sup>11</sup> A. B. Bestul and D. J. Salley, American Cyanamid Company Technical Data Sheet (Dec., 1947).
- <sup>12</sup> L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1939), pp. 53 and 123.

## On Rotation in Ammonium Halides

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October 18, 1948

ALTHOUGH thermodynamic evidence<sup>1</sup> has been obtained which is opposed to the notion that the phase transition in  $\text{NH}_4\text{Cl}$  is due to the onset of free rotation of the  $\text{NH}_4^+$  ions, Beck's grating studies<sup>2</sup> of the  $1750\text{-cm}^{-1}$  bands in the infra-red spectra of  $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{Br}$  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  $\text{ND}_4\text{Cl}$  in the temperature range,  $28^\circ\text{C}$  to  $-190^\circ\text{C}$ , and find no evidence of rotational structure in any of the salts in either phase. The  $1750\text{-cm}^{-1}$  band obtained with  $\text{NH}_4\text{Cl}$  is shown in Fig. 1. The spectra of the other salts are similar,

FIG. 1. 5.6  $\mu$  band of  $\text{NH}_4\text{Cl}$ .

Our resolution in this region was better than  $5\text{ cm}^{-1}$  and the reported rotational spacing was about  $15\text{ cm}^{-1}$ .

It seems clear that the structure previously obtained was due to water vapor. Although the peaks reported do not coincide with water vapor peaks, the approximate separation is the same and we have observed that in spectra taken point by point apparent peaks are frequently obtained on the steep sides of lines in the background spectrum. Furthermore, it is noteworthy that although the band center in the bromide occurs at a frequency  $50\text{ cm}^{-1}$  lower than in the chloride, peaks were reported at identical frequencies in both spectra.

Our data show no evidence of rotation in either phase. We have been able to interpret the major features of the low temperature infra-red spectrum of  $\text{NH}_4\text{Cl}$  on the basis of a body-centered lattice in which all  $\text{NH}_4^+$  tetrahedra are similarly oriented, and the  $\text{NH}_4\text{Br}$  spectrum on the basis of a similar structure in two dimensions but with a screw axis replacing translation in the third dimension (i.e., space group  $D_{4h}^8$ ). The splitting of the triply degenerate mode at  $1400\text{ cm}^{-1}$  constitutes our chief evidence. These structures are both in accord with optical, piezoelectric, x-ray and Raman data obtained on these crystals.<sup>3</sup> The fact that the spectra of the room temperature phases of the two compounds are almost identical suggests that the room temperature modification of both salts has the same structure, in which the  $\text{NH}_4^+$  ions are randomly distributed between the two possible orientations, and that the phase transition is a simple order-disorder transition.

Experimental work on  $\text{ND}_4\text{Br}$  is in progress and more detailed data and analysis will be published shortly.

<sup>1</sup> A. W. Lawson, Phys. Rev. **57**, 417 (1940).

<sup>2</sup> C. Beck, J. Chem. Phys. **12**, 71 (1944).

<sup>3</sup> A. C. Menzies and H. R. Mills, Proc. Roy. Soc. (London) **148**, 407 (1935). These data are conveniently summarized in this article. However, the  $\text{NH}_4\text{Br}$  model used by these authors does not account for the splitting of the  $1400\text{-cm}^{-1}$  mode.

## Physical Adsorption on Non-Uniform Surfaces

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November 11, 1948

IN a recent paper<sup>1</sup> with the above title, G. Halsey has discussed several aspects of adsorption including the BET theory and "cooperative adsorption." The writer would like to make a few comments on these two points.

Halsey makes the following statement which, it seems to the writer, may lead to some confusion: "...the hypotheses of the BET theory lead to substantially no adsorption beyond the first layer if  $E_2 = E_L$ , and stepwise isotherms if  $E_1 > E_2 > E_3 \dots > E_L$ ." Now actually the hypotheses of the BET theory<sup>2</sup> lead, as is well known, to multimolecular adsorption for any value of the BET constant  $c$  for  $p/p_0$  sufficiently close to unity, and in no case to stepwise isotherms. Halsey's statement actually refers to a mixture of BET hypotheses and somewhat refined hypotheses. In summary, although the BET model assigns extremely unrealistic properties<sup>2</sup> to the liquid state, the model *does* lead to multimolecular adsorption. The present writer, in other words, is by no means defending the BET model, but is defending the deductions which have been made from the model.

Halsey discusses cooperative adsorption (i.e., adsorption in which horizontal as well as vertical interactions are taken into account so that condensation phenomena are possible<sup>2</sup>) and in this connection accepts the reality of stepwise adsorption near the surface—although he feels that the non-uniform nature of the surface will tend to smooth out these steps. This is a new and interesting point of view. It should be pointed out, however, that a closely related approximate quantitative approach to the problem of "cooperative" adsorption on a uniform surface (for mathematical simplicity) has already been given,<sup>3</sup> though not mentioned by Halsey in his discussion of cooperative adsorption. Stepwise adsorption was encountered in the mathematical equations and was discussed, although it was not felt that the model was sufficiently refined to come to a definite conclusion concerning the physical significance of this aspect of the approximate theory.

<sup>1</sup> G. Halsey, J. Chem. Phys. **16**, 931 (1948).

<sup>2</sup> These can probably be outlined most clearly in terms of a statistical mechanical model. See: (1) T. L. Hill, J. Chem. Phys. **14**, 263 (1946), Eqs. (3)-(5), (28) (29), and Fig. 1; (2) J. Chem. Phys. **15**, 767 (1947), Eq. (18).

<sup>3</sup> T. L. Hill, J. Chem. Phys. **15**, 767 (1947).

## A New Equation for the Non-Stationary Shock Wave

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November 2, 1948

IN analogy to the "Stoßpolare" of Busemann<sup>1</sup> for the stationary shock wave of two dimensions I found an equation for the non-stationary shock wave of one dimension.

We start from the well-known hydrodynamic equations

$$(w-u)\rho = (\rho-\bar{u})\bar{p}, \quad (1)$$

$$(w-u)^2\rho + p = (w-\bar{u})^2\bar{p} + \bar{p}, \quad (2)$$

$$\frac{a^2}{u-1} + \frac{(w-u)^2}{2} = \frac{\bar{a}^2}{u-1} + \frac{(w-\bar{u})^2}{2},$$

where  $w$  is the speed of the shock wave,  $u$  the velocity of the gas,  $\rho$  the density,  $p$  the pressure,  $a$  the velocity of sound, and  $a^2/u-1=i$ , the enthalpy of a perfect gas; the bar refers to the quantities behind the shock wave. By