Summary

1. A fairly large number of salts, especially halides and nitrates, have been found to be soluble in acetic acid. All sulfates are very slightly soluble.

2. Double decomposition reactions have been found to take place quite readily in this solvent. A number of such reactions have been described.

3. Solvolysis does not occur in acetic acid solutions to any marked extent.

4. Analogies have been pointed out between the behavior of certain acetates in acetic acid and that of the corresponding hydroxides in water.

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THE MOLECULAR HEAT AND ENTROPY OF HYDROGEN CHLORIDE CALCULATED FROM BAND SPECTRA DATA

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I. Introduction

It is well known that the heat capacity of gases decreases with temperature in the neighborhood of absolute zero. The temperature variation of the molecular heat of gaseous hydrogen chloride is especially interesting because it may be used to confirm the interpretation which the new quantum mechanics places upon band spectra. The computation of molecular heats, by means of the energy levels derived from band spectra, was first carried through by Hicks and Mitchell.[1] They made use of the spectral measurements of Imes and of Colby, Meyer and Bronk and assumed the "*a priori* probabilities" or weights of the quantum states to be 2, 4, 6, 8, etc., corresponding to those states characterized by the rotational quantum numbers $^1/_2$, $^3/_2$, $^5/_2$, $^7/_2$, etc. Van Vleck[2] and others have pointed out that according to the new quantum mechanics the *a priori* probabilities must be 1, 3, 5, 7 for the states $^1/_2$, $^3/_2$, $^5/_2$, $^7/_2$ for simple polar molecules like HCl. Experimental proof that these probabilities are correct is furnished by Bourgin's[3] measurements of the absorption intensities of hydrogen chloride.

The band spectra measurements of Colby, Meyer and Bronk have been recalculated by Kemble,[4] who has obtained equations expressing the energy levels as a function of the vibrational and rotational quantum numbers.

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[1] Hicks and Mitchell, THIS JOURNAL, **48,** 1520 (1926).

[2] Van Vleck, *Phys. Rev.*, **28,** 986 (1926); see also Hutchisson, *ibid.*, **29,** 360A (1927).

[3] Bourgin, *ibid.*, **29,** 794 (1927).

[4] Kemble, *J. Opt. Soc. Am.*, **12,** 1 (1926).

The calculations made in this paper are based on Kemble's values for the energy levels and the *a priori* probabilities assigned by the new mechanics. Besides the molecular heats, the entropy values of hydrogen chloride at the various temperatures are calculated in accordance with the method given by Giauque and Wiebe.[5] The calculated results are then compared with experiment.

II. Calculations

The molecular heat of a gas is obtained by differentiating the energy of a mole of the gas with respect to the temperature. The translational energy of the gas remains constant and may therefore be left out of consideration. The rotational and vibrational energy may be obtained by summing up the different energy levels obtained from band spectra data. The expression for the molecular heat is well known and has been used by several investigators. It may be written as

$$C = \frac{N}{J}\frac{d}{dT}\frac{\Sigma_n\Sigma_m\, p^n_m\, W^n_m\, e^{-\frac{W^n_m}{kT}}}{\Sigma_n\Sigma_m\, p^n_m\, e^{-\frac{W^n_m}{kT}}}$$

where p^n_m is the *a priori* probability of the m^{th} rotational state and the n^{th} vibrational state, J is the mechanical equivalent of heat and N is Avogadro's number. For purposes of computation a more convenient form is as follows

$$C = \frac{Nk}{J}\left[\frac{P_3}{P_1} - \left(\frac{P_2}{P_1}\right)^2\right]$$

in which

$$P_i = \Sigma_n\Sigma_m\, p^n_m\, (\sigma^n_m)^{(i-1)}\, e^{-\sigma^n_m} \text{ and } \sigma^n_m = \frac{\epsilon^n_m\, ch}{kT}$$

where e^n_m are the band spectra wave numbers expressed in cm.$^{-1}$.

Kemble's equations for the spectral energy levels may be written[6] (expressed in cm.$^{-1}$)

$$F_m(m) = A_n + 2\delta\, m + B_n\, m^2 + D_n\, m^4$$

where

$$\begin{array}{lll}
A_0 = 0 & B_0 = 10.4469 \pm 0.0050 & D_0 = -0.000529 \\
A_1 = 2887.19 \pm 0.053 & B_1 = 10.1417 \pm 0.0050 & D_1 = -0.000522 \\
A_2 = 5667.23 \pm 0.17 & B_2 = 9.8624 \pm 0.0023 & D_2 = -0.000514
\end{array}$$

and $\delta = 0.078 \pm 0.012$. In the 600° K. calculation 28 terms for $n = {}^1/_2$, 24 terms for $n = {}^3/_2$, and 12 terms for $n = {}^5/_2$, are needed. In these calculations m takes the value ${}^1/_2$, ${}^3/_2$, ${}^5/_2$, ${}^7/_2$, etc.

The results of the computations are given in Table I. The constants used in all the results are those found in the "International Critical Tables."

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[5] Giauque and Wiebe, THIS JOURNAL, **50**, 101 (1928).

[6] In this equation our m is the same as Kemble's $(j - {}^1/_2)$.

The probable error in the value of molecular heat may be indicated by making use of the probable errors assigned to the band spectra constants by Kemble. For instance, in the computation for 0° (273.1°K.) the B_0 term is the major portion of important energy levels so that the percentage probable error remains constant for all terms. A change may therefore be made in the temperature which will balance the change in ϵ_m^n and still keep σ constant. The required change in temperature is ± 0.13°K. This change in temperature would produce a change of only a few units in the fifth decimal place. Kemble's constants and therefore the molecular heats are given for the lighter isotope of HCl. The change produced by the other isotope would be very small.

TABLE I

RESULTS OF COMPUTATIONS

T, °K.	C(Rot. + Vib.) cal. deg.$^{-1}$ mole^{-1}	C_v cal. deg.$^{-1}$ mole^{-1}	$\int_0^T C/T\,dT$ Entropy units per mole
600	2.1010	5.0814	9.354
450	2.0182	4.9986	8.761
373.1	2.0023	4.9827	8.385
273.1	1.9962	4.9766	7.761
200	1.9945	4.9749	7.140
120	1.9933	4.9737	6.121
60	1.9954	4.9758	4.739
30	2.0110	4.9914	3.352
15	2.1386	5.1190	1.928
13	2.1782	5.1586	1.619
11	2.1630	5.1434	1.255
8	1.7235	4.7039	
6	0.9517	3.9321	
5	.5140	3.4944	
4	.1799	3.1603	
3	.0259	3.0063	
1	.0000	2.9804	

In Fig. 1 the molecular heats are plotted against the temperature.[7] This graph shows the sharp maximum which occurs at about 12.5°K. The shape of this curve is markedly different from the experimental molecular heat–temperature curve for hydrogen, which has a gradual monotonic increase in C_v from $^3/_2\ R$ at 60°, to approximately $^5/_2\ R$ at room temperature. The explanation[8] of the absence of a maximum on the basis of the quantum theory in the case of hydrogen, is that the gas is made up of a mixture of molecules of different types (those having symmetrical and those having antisymmetrical "eigenfunctions"). The molecular heat of this mixture gives a curve which agrees well with experiment at low temperatures.[9]

There are not many accurate determinations of the molecular heat of gaseous hydrogen chloride. Observations have been made by Masson,[10]

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[7] It should perhaps be noted that these calculations take no account of the Van der Waals forces. However, the experimental values have been reduced to the ideal state so that the calculated values should agree with experiment. The possible existence of $(HCl)_2$ molecules has been neglected.

[8] Dennison, *Proc. Roy. Soc.* (*London*), **115A**, 463 (1927).

[9] Cornish and Eastman, THIS JOURNAL, **50**, 627 (1928).

[10] Masson, *Phil. Mag.*, **13**, 533 (1857).

Regnault,[11] Strecker[12] and Muller,[13] but their values disagree among themselves so much that it is difficult to have much faith in any of them. Pier[14] measured the molecular heat of HCl from 0 to 1600°, using the bomb method, and obtained the equation $C_v = 4.90 + 0.0009\ \Theta$, where Θ is the centigrade temperature. The values obtained from his equations are included in Fig. 1. Pier's data for hydrogen appear to be too low at room temperature, so it is possible that the same is true for hydrogen chloride.

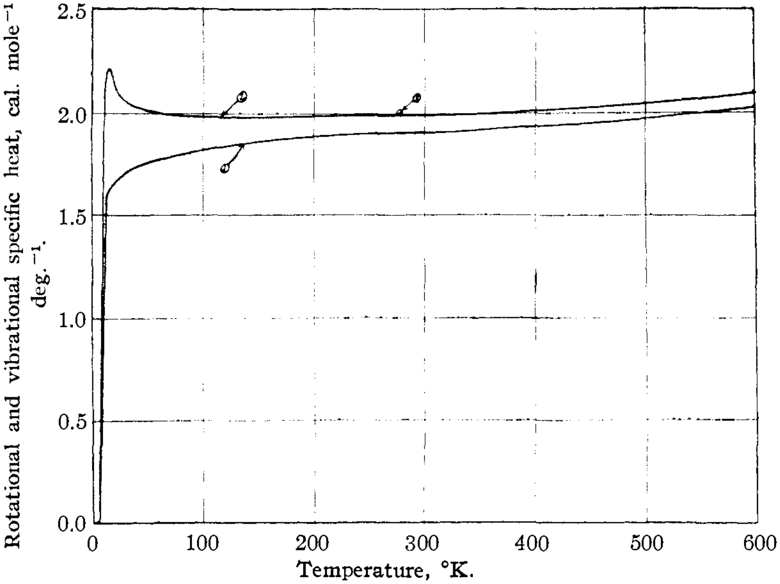

Fig. 1.—Graph showing the variation of the specific heat of hydrogen chloride with temperature calculated from band spectra data. Curve 1 is taken from Hicks and Mitchell's data. Curve 2 shows the values calculated in this paper based upon the *a priori* probabilities indicated by experiment and the new quantum mechanics. The single reliable experimental point is shown at (3).

The most accurate measurements are, without doubt, those of Schweikert,[15] using the velocity of sound method. His values have been slightly corrected by Partington and Schilling.[16] His value for C_v at 0° is 4.995 cal. mole^{-1} deg.$^{-1}$, which agrees well with the calculated value ($C_v = 4.977$) given, and certainly confirms this result rather than the calculated value of $C_v = 4.879$ on the basis of the older quantum mechanics.

[11] Regnault, *Mem. Acad.*, **26**, 1 (1862).

[12] Strecker, *Wied. Ann.*, **13**, 20 (1881); **17**, 85 (1882).

[13] Muller, *ibid.*, **18**, 94 (1883).

[14] Pier, *Z. physik. Chem.*, **66**, 759 (1909); Nernst, *Z. Electrochem.*, **17**, 272 (1911).

[15] Schweikert, *Ann. Physik*, **48**, 593 (1915).

[16] Partington and Schilling, "Specific Heat of Gases," Ernst Benn, Ltd., London, **1925**.

Giauque and Wiebe have shown that the same terms used for specific heats may be used to evaluate $\int_0^T C/TdT$ for entropy calculations. In our notation their equation may be written

$$S_2 = \int_0^T CT/dT = R\left[\ln P_1 - \frac{P_2}{P_1}\right]$$

The values of this integral for the various temperatures are included in Table I. The total entropy may then be obtained by using the Sackur equation for the entropy due to the translational energy

$$S_1 = \frac{3}{2} R \ln M + \frac{3}{2} R \ln T + R \ln V + S_0$$

where S_0 has the values -11.06 (Tetrode) or -11.38 (Lewis) entropy units per mole. Giauque and Wiebe have given, as the experimental value of the entropy per mole, 41.2 Entropy Units at the boiling point (188.07°K.). Extrapolating between the values given in Table I, we obtain $S_2 = 7.02$ at 188.07°K. Using the values given in the "International Critical Tables," S_1 is found to be 34.35 or 34.03, depending upon the value of S_0. Our value for the total entropy per mole at the boiling point is therefore 41.45 or 41.13 E. U., while the experimental value given by Giauque and Wiebe is 41.3 when corrected to the ideal state. At 298.1°K. our calculated value of the entropy is 44.65 or 44.33, while the experimental value is given as 44.5. The calculated values at 298.1°K. are 0.01 E. U. higher than those given by Giauque and Wiebe. At 0° the total entropy per mole amounts to 44.04 or 43.72 E. U.

If we make use of the value of S_2 taken from Hicks and Mitchell's data, which is given as 6.75 at 298.1°, we may compare the entropy results of the older quantum theory with those of the new mechanics. It was noted by Giauque and Wiebe that Hicks and Mitchell neglected the zero point entropy. It may also be noted that Hicks and Mitchell have an error in summing up the components of the entropy, S_1 and S_2, to obtain their final entropy value in the case that uses the Tetrode constant. Using S_2 as given, the entropy per mole at 298.1°K. is 44.85 or 44.53 E. U. as compared with the experimental value of 44.5 E. U. In this case, also, the present calculations give slightly better agreement than those based on the older quantum theory, although the agreement is not decisive because of the large probable error in the experimental result.

Summary

The molecular heat of gaseous hydrogen chloride is computed from band spectra data for temperatures from 1°K. to 600°K. It is shown that the curve obtained by plotting the molecular heat against temperature rises to a maximum at 12.5°K. At 0° the calculated molecular heat agrees very well with the single reliable experimental value, while the earlier calculations of Hicks and Mitchell give a value about 0.1 cal. mole^{-1} deg.$^{-1}$ too low.

The values of $\int_0^T C/TdT$, which may be used to calculate the entropy

for the various temperatures, are calculated by the method suggested by Giauque and Wiebe. The entropy at 0° is found to be 44.04 or 43.72 Entropy Units per mole, depending upon whether the Tetrode or Lewis value of the chemical constant is used.

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A RAPID METHOD FOR THE SEPARATION OF ALUMINUM AND BERYLLIUM

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From the voluminous literature on the subject of the separation of aluminum and beryllium it may be concluded that the estimation of these elements in the presence of each other is of great difficulty, and that there is no simple, satisfactory method for their accurate determination. An excellent summary of the older methods for the separation of aluminum and beryllium will be found in C. L. Parsons' "The Chemistry and Literature of Beryllium." H. T. S. Britton[1] concluded from an experimental study of the more important methods proposed that the only four which were capable of giving satisfactory results, if the details of the respective procedures were carefully adhered to, were the following. 1. Decomposition by boiling of sodium hydroxide solutions of aluminum and beryllium.[2] Sodium beryllate is hydrolytically decomposed, giving a precipitate of beryllium oxide; sodium aluminate remains in solution. 2. Parsons and Barnes' method.[3] Beryllium hydroxide is dissolved by hot sodium bicarbonate solution; aluminum hydroxide is not dissolved. 3. Method of Wunder and Wenger.[4] The oxides are fused with sodium carbonate and the residue is extracted with water. Aluminum goes into solution. 4. F. S. Havens'[5] ether–hydrochloric acid method. Beryllium chloride alone is soluble in a mixture of hydrochloric acid and ether saturated with hydrogen chloride. Of these methods, Britton considered 1 and 4 to be the most satisfactory. For discussion and criticism of these methods, see Hellmut Fischer[6] and also L. Moser and M. Niessner.[7] A method which appears to be superior to any hitherto proposed has recently

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[1] Britton, *Analyst*, **46**, 359, 437 (1921); **47**, 50 (1922).

[2] R. Gmelin and Schaffgotsch, *Pogg. Ann.*, **83**, 175 (1843); Penfield and Harper, *Am. J. Sci.*, (iii), **32**, 110 (1886); Zimmermann, *Z. anal. Chem.*, **27**, 61 (1888).

[3] Parsons and Barnes, THIS JOURNAL, **28**, 1589 (1906).

[4] Wunder and Wenger, *Z. anal. Chem.*, **51**, 470 (1912).

[5] Havens, *Z. anorg. Chem.*, **16**, 15 (1898).

[6] Fischer, "Wissentschaftliche Veröffentlichungen aus dem Siemens-Konzern," **1926**, Band V, Heft 2, p. 99.

[7] Moser and Niessner, *Monatsh.*, **48**, 113 (1927).