On The Nature of The Liquid State

William Band

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The most successful attempts, empirically, at developing a theory of liquids in terms of van der Waals forces, are based on the concept of a free volume of atomic dimensions in which each molecule is free to wander under the influence only of its nearest neighbors.[1] Essentially this is an artificial device to permit the use of a gas type of partition function, while at the same time ensuring that the external pressure on the assembly needs to have only small values compared with those which would be required to keep a gas at the same density.

There is a classical and theoretically much more acceptable device for accomplishing exactly this result, namely the intrinsic pressure of Laplace.[2] In modern language, the van der Waals forces build up a potential well within the liquid. Using methods familiar in metal theory, this well can be smoothed out, leaving only the potential wall at the boundary. Within this wall the molecules are free to behave as a gas of spheres with non-negligible size. Only those molecules whose kinetic energy is greater than the height of the wall will contribute to the external pressure.

Assuming the van der Waals forces are similar to those found by Lennard-Jones,[3] the mean potential per molecule will rise with increasing temperature because greater kinetic energy will carry molecules further up into regions of positive potential of interaction with its neighbors. But there exists for these forces an optimum density at which the potential has a greatest depth. If T_c is the temperature at which for this optimum density the mean potential per molecule just vanishes, then for T greater than T_c no density can be found for which the potential is negative. The liquid cannot exist as a separate phase at such temperatures.

For T less than T_c it is always possible to find a density near enough to the optimum value to form a potential well in which at least some of the molecules can be trapped by what is thus equivalent to an intrinsic pressure.

If the liquid is in contact with its own vapor, the saturated density of the latter can easily be calculated as an equilibrium problem. The liquid density has to adjust itself to the vapor pressure, reacting as a gas to the sum of this pressure and the intrinsic pressure.

The liquid-vapor change on this picture is consistent with Mayer's rigorous treatment,[4] and with the clustering picture developed since.[5] The present picture illuminates the process of freezing as follows. The liquid phase exists when the density is such that the van der Waals forces *integrate to produce a potential well in which the molecules can float as units*. At greater densities, the molecular collisions become so intimate that the electron shells are seriously disturbed. Finally there will be a critical density at which the coupling between the molecular core and the outer shell is broken; there will then be a sudden transition from intramolecular coupling between core and shell, to intermolecular coupling between cores on the one hand and shells on the other. This gives the picture of the crystalline state developed by Shockley,[6] in which the cores float as a lattice in a potential well caused by the charges on the electron gas.

The detailed analysis required for the complete elucidation of this picture of the liquid state is now being undertaken.

WILLIAM BAND

Yenching University,
Peiping, China,
September 26, 1939.

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The Heat Capacity of Cyanogen Gas

We have determined the heat capacity of cyanogen gas using the adiabatic expansion method of Lummer and Pringsheim. Pure nitrogen was used as the standard comparison gas, its heat capacity being calculated from spectroscopic data. Two different samples of cyanogen were used, each of which was prepared from copper sulphate and potassium cyanide. Care was taken to free the gas from hydrogen cyanide, water, and carbon dioxide. In Table I the experimental molal heat capacities at constant pressure, obtained at three different temperatures, are given. The values of $C_P{}^0$ are those for the gas at infinite attenuation.

The theoretical heat capacities in column three were calculated from the vibrational frequency assignment of Woo and Badger,[1] which gives the following values for the frequencies: $\nu_1 = 860$ cm^{-1}, $\nu_2 = 2150$ cm^{-1}, $\nu_3 = 2336$ cm^{-1}, $2\delta_1 = 230$ cm^{-1}, and $2\delta_2 = 512$ cm^{-1}. This assignment is in accord with the entropy data of Ruehrwein and Giauque,[2] and, as pointed out by Stevenson,[3] the frequency ν_1 is in agreement with the electron diffraction studies of Pauling, Springall and Palmer.[4] Eucken and Bertram,[5] as a result of their heat capacity measurements by the hot wire method, assigned a value of 740 cm^{-1} to the $2\delta_1$ vibration, but this value is certainly too high. The lower value, 230 cm^{-1}, has been confirmed recently by the work of Bailey and Carson[6] on the infra-red spectrum of the gas.

In the calculation of the experimental heat capacities $P = RT/(V - B_0)$ was used as the equation of state. The virial coefficients B_0 were calculated from the relation $B_0 P_c/T_c = \beta_\theta - A/\theta - C/\theta 3$ given by Keyes,[7] where $\theta = T/T_c$. The values of the constants β_θ, A_θ and C_θ used for cyanogen were assumed to be the averages obtained by Keyes from eleven different nonpolar gases. It must be remembered that the values of B_0 for cyanogen obtained in this way may be in error by as much as 20 percent. The true values of B_0 are probably numerically greater than those given by

TABLE I.

TEMPERATURE (°A)	$C_P{}^0$ OBSERVED (CAL./DEG.)	$C_P{}^0$ CALCULATED (CAL./DEG.)	PERCENT DEVIATION FROM THEORY
273.16	13.14 ± .02	13.18	−.31
296.36	13.46 ± .02	13.53	−.52
326.91	13.96 ± .02	13.95	+.07

the Keyes relation. This may well account for a part of the small discrepancies between the experimental and calculated values at the lower temperatures.

Recently Stitt[8] has communicated values of C_v^0 for cyanogen as obtained by an improved "hot wire" thermal conductivity method. His values are from 2 percent to 4 percent higher than those predicted by theory, but, like those presented here, they are in essential agreement with the theoretically predicted heat capacities. The values of C_v^0 obtained by Eucken and Bertram, on the other hand, are over 20 percent less than those reported by Stitt and by us, and a frequency of $2\delta_1 = 740$ cm^{-1} rather than 230 cm^{-1} was required to get agreement with theory.

E. J. BURCIK
DON M. YOST

Gates and Crellin Laboratories of Chemistry,
California Institute of Technology,
Pasadena, California,
October 28, 1939.

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The Heat Capacity of Cyanogen Gas

The object of this note is to report three measurements of the heat capacity of cyanogen gas made several months ago on the "hot wire" thermal conductivity apparatus[1] at Harvard University. At that time it was intended to later study the infra-red spectrum of cyanogen and perhaps make more measurements of the heat capacity. Since this additional work has been indefinitely postponed, the earlier results are reported now.

The bracketing procedure already described[1] was employed. When a platinum black wire was used, it was found that the ratio of the thermal conductivity of cyanogen to that of ethylene under the same conditions was greater than with a bare platinum wire, whereas the opposite was found to be true when cyanogen was similarly compared to acetylene. This indicates[1] that the accommodation coefficient of cyanogen is intermediate between those of ethylene and acetylene, that is $\alpha_{C_2H_4} > \alpha_{C_2N_2} > \alpha_{C_2H_2}$. Upper and lower limits to the heat capacity of cyanogen found from the thermal conductivity data assuming that

TABLE I. *The heat capacity of cyanogen gas.*

T (°K)	EXPERIMENTAL C_v^0 (CAL./MOLE-DEGREE)		CALCULATED C_v^0 (CAL./MOLE-DEGREE)
185.2	9.61	9.59	9.41
294.1	12.05	12.04	11.54
320.4	12.42	12.29	11.91

$\alpha_{C_2H_2} = \alpha_{C_2H_2}$ and that $\alpha_{C_2N_2} = \alpha_{C_2H_4}$ are shown in columns 2 and 3, respectively, of Table I. These values are for the gas at 0.01 mm pressure, or essentially for the ideal gas. Values of the heat capacity of acetylene were calculated using harmonic vibrational frequencies 612(2), 729(2), 1973, 3283, and 3372 cm^{-1}; values for ethylene were taken from Eucken and Parts.[2] The experimental error of the thermal conductivity data is believed to be less than 1 percent.

The values of the heat capacity of cyanogen reported in Table I are not at all in agreement with those found by Eucken and Bertram[3] by the "hot wire" method on the assumption that argon and cyanogen have the same accommodation coefficient. Recent adiabatic expansion measurements by Burcik and Yost[4] lead to values in essential agreement with those reported here, so there is little doubt that the earlier values are in error. This conclusion was also suggested by Woo[5] on the basis of force constant considerations.

A study of the available spectroscopic data[6] on cyanogen indicates that Mecke's assignment[7] of the fundamental frequencies is probably correct. The frequencies used in calculating the figures in column 4 of Table I are 230(2), 510(2), 850, 2150, and 2330 cm^{-1}. The last four of these are definitely established from the infra-red and Raman data and the selection rules. The value of the lowest frequency is the most doubtful, although its determination[6(c)] from the ultraviolet spectrum seems rather reliable. The calculated values of Table I differ from the experimental by considerably more than the estimated experimental error. It is not certain at present whether this disagreement is due to larger error in the experimental values or at least partly to an error in the calculated values. If the contributions to the heat capacity of all but the lowest of the frequencies are assumed to be correctly calculated using the harmonic frequencies listed, a contribution of slightly over 1.99 cal./mole-degree for the lowest frequency is needed to bring the observed and calculated values into perfect agreement at the higher temperatures. This suggests that the calculated values might be appreciably higher if anharmonicity could be adequately taken into account.

I wish to thank Mr. Debeau for preparing the cyanogen used in this work. It was prepared by the usual method.[8]

FRED STITT*

Chemistry Department,
Indiana University,
Bloomington, Indiana,
October 21, 1939.

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* This work was done while the author was a National Research Fellow in Chemistry at Harvard University.