

Some Heat Capacity Data for Liquid Nitrobenzene; No Indication of Allotropy

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Citation: *The Journal of Chemical Physics* **2**, 440 (1934); doi: 10.1063/1.1749503

View online: <http://dx.doi.org/10.1063/1.1749503>

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LETTERS TO THE EDITOR

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Some Heat Capacity Data for Liquid Nitrobenzene; No Indication of Allotropy

The suggestion that nitrobenzene exists in two different liquid forms with a transition point at about 9.6°C has been made by Mazur and his collaborators.¹ They have published experimental data which indicate that the density and dielectric constant show discontinuities in the neighborhood of this temperature and from a heating curve they have estimated the heat of transition to be 0.14 calorie per gram. They also state that the heat capacity of the liquid below 9.6° is considerably less than that above this temperature. Other investigators,² however, have failed to find evidence of such discontinuities in studies of the density, refractive index, dielectric constant, surface tension and several other properties of nitrobenzene.

In connection with an investigation of the entropies of some representative organic compounds containing nitrogen we have recently measured the heat capacity of liquid nitrobenzene over a continuous range from 0° to 26°C. The determinations were made by the Nernst method with an aneroid calorimeter³ and represent average specific heats for temperature intervals of only 3° or 4°. While the systematic errors in the results thus obtained may possibly have been as great as 0.6 percent, the fortuitous errors, which are the important ones in the present argument, were certainly less than 0.30 percent in all cases. The sample of nitrobenzene employed was obtained from a C. P. Eastman material by eight successive fractional crystallizations. Its melting point, determined both by a copper-constantan thermocouple in the course of the heat capacity measurements and by a mercury thermometer

which had been calibrated by the U. S. Bureau of Standards, was 5.65° ($\pm 0.05^\circ$).

Our experimental results are given in columns 1 and 2 of Table I and are also represented graphically in Fig. 1. As can be readily seen, they deviate only very slightly and in a

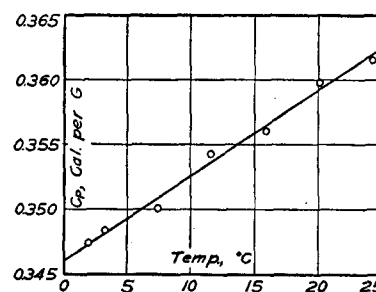


FIG. 1. A plot of the specific heat data for liquid nitrobenzene.

fortuitous manner from the straight line which represents the equation, $C_p = 0.3460 + 0.00066t$. The values calculated by this equation are also given in the third column of the table in order to facilitate comparison with the experimental data. The liquid can be readily cooled several degrees below the freezing point and the first two experimental results refer to measurements made upon our sample in this undercooled condition.

TABLE I. *Specific heat data for liquid nitrobenzene.*

Average Temp. (°C)	C_p observed (cal./g)	C_p calculated (cal./g)
1.95	0.3474	0.3473
3.30	0.3484	0.3482
7.42	0.3501	0.3509
11.60	0.3543	0.3537
15.94	0.3561	0.3565
20.11	0.3598	0.3593
24.25	0.3616	0.3620

¹ (a) Mazur, *Nature* **126**, 993 (1930); **127**, 741, 893 (1931); *Acta. Phys. Pol.* **1**, 53 (1932); (b) Wolfke and Mazur, *Zeits. f. Physik* **74**, 110 (1932); *Acta Phys. Pol.* **1**, 71 (1932); (c) Wolfke and Ziemecki, *Acta. Phys. Pol.* **1**, 271 (1932).

² Lind and Young, *J. Chem. Phys.* **1**, 266 (1933); Wellm, *Zeits. f. physik. Chemie* **B19**, 113 (1932); Cohen and te Boekhorst, *Proc. Acad. Sci. Amsterdam* **35**, 1016 (1932).

³ Parks, *J. Am. Chem. Soc.* **47**, 338 (1925).

It is quite evident that our heat capacity results show no discontinuity in the neighborhood of 9.6° and no sign of a heat of transition. In our procedure the latter would naturally have been included in either the measurement corresponding to an average temperature of 7.4° or that for 11.6° , as the series of measurements left no temperature gaps between 0° and 26° . Therefore we can see no basis for

the claim that pure nitrobenzene exists in two allotropic liquid forms.

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May 11, 1934.

The Significance of the Activation Energy of Collision

Acoustical measurements have established that the rate of vibrational energy exchange is in general strongly dependent on temperature.¹ In order to describe this the term "activation energy of collision" has been employed,² and this quantity appears to be of the order of one to three $h\nu$ where ν is the vibration frequency of the molecules in the experiments so far reported. I wish to report in this letter the preliminary result of a theoretical investigation which has attempted to give the "activation energy of collision" a more precise significance.

At first the excited and exciting molecules were considered held at a fixed distance, and then the relative kinetic energy was allowed to enter as a perturbation giving rise to an exchange of translational and vibrational energy. This led to two simultaneous differential equations for the eigenfunctions of the excited and the unexcited molecules. To solve these to a first approximation plane wave functions which vanished inside the kinetic theory diameter were introduced. This permitted a comparison between the outward flow of excited molecules with a normalized incoming wave of unexcited molecules. This gave for a collision energy E a probability for the exchange of a vibrational quantum proportional to $E^{1/2}(E - H\nu)^{5/2}$. This treatment differs from that given by Rice³ in that the wave function of the internal coordinates includes as a parameter, a fixed value of the distance of separation due to the clamping of the molecules. It obviates as well the paradoxical approximation of adiabatic approach implied in

an extension of the treatment of Kallman and London^{2, 4} to the conversion of translational into vibrational energy.

When integrated over all energies the temperature dependence of the yield is nearly proportional to the fourth power of the temperature times the usual factor $e^{-h\nu/kT}$. Expressed as an activation energy this is approximately $4kT$, which agrees well with the experimental values for carbon dioxide, carbon disulfide, etc. The second order effects such as the softening of the bonds at close approach, the effect of repulsion on the eigenfunctions previous to the point where they vanish, and the shielding by other atoms in polyatomic molecules would tend to increase this temperature dependence. The absolute magnitude of the yield was of the order of 10^{-4} – 10^{-7} per collision depending upon the type of molecule. This is also in agreement with experiment.

HILLARD B. HUNTINGTON

Princeton University,
Princeton, New Jersey,
June 1, 1934.

¹ Henry, Proc. Camb. Phil. Soc. **28**, 249 (1932); Richards and Reid, Nature **130**, 739 (1932); J. Chem. Phys. **2**, 193, 206 (1934).

² Richards, J. Chem. Phys. **1**, 874 (1933).

³ Rice, J. Am. Chem. Soc. **54**, 4559 (1932).

⁴ Kallman and London, Zeits. f. physik. Chemie **B2**, 207 (1929).

Photo-Dissociation of the Vapors of Organo-Metallic Compounds

The photochemistry of the simplest organo-metallic compounds of the type MR_n (M =metal, R = CH_3 , C_2H_5 , C_6H_5) has not as yet received due attention. Only one observation may be cited, namely that of Berthelot and Gaudechon,¹ who found that liquid $Zn(C_2H_5)_2$ illuminated by a quartz mercury arc decomposes rapidly into ethane and zinc metal. We expect in fact that less energy is needed to disrupt the bond $M-C$ than the bond $C-C$; therefore photochemical reactions can be induced by smaller quanta such as those lying in the nearer ultraviolet.

A study of these compounds was therefore undertaken in this laboratory. Some of the results obtained are given here.

First, the absorption spectra of $Hg(CH_3)_2$, $Zn(CH_3)_2$ and $Pb(C_2H_5)_4$ were studied. These substances are very volatile. A structure in the absorption spectrum of $Hg(CH_3)_2$ could be detected only when this liquid was frozen down to

$-150^\circ C$. At room temperature the vapor pressure is so high that all the ultraviolet is completely absorbed.

The absorption spectrum of $Hg(CH_3)_2$ consists of a progression of diffuse bands in the region 2100–1970 Å. The spacing of these bands is equal to 350 cm^{-1} and represents presumably the vibration quantum of one of the valence modes of vibration of the mercury atom in the upper electronic state of the molecule. From the Raman spectrum the valence vibration frequencies of the Zn atom in the ground state of the $Zn(CH_3)_2$ molecule are known to be 506 and 617 cm^{-1} .² For $Hg(CH_3)_2$ no corresponding data are available, but the order of magnitude must be the same.

The electronic transition in the $Hg(CH_3)_2$ molecule is equal to $47,044\text{ cm}^{-1}$ or 5.8 e.v.

¹ Berthelot and Gaudechon, C. R. **156**, 1245 (1913).

² S. Venkateswaran, Ind. J. Phys. **5**, 145 (1930).