mended gravimetric and volumetric methods should agree within experimental error. In fact, the results are in better agreement than could be expected, for one drop of the 0.1 N solution of permanganate that was used in the volumetric method represented 0.3 mg. of uranium.

TABLE VI

COMPARISON OF RESULTS OBTAINED BY WEIGHING AS U_3O_8 AND BY REDUCTION AND TITRATION

Expt.	1	2	3	4	5
U obtd. by weighing as U_3O_8, g.	0.0965	0.0963	0.2983	0.2982	0.2983
By reduction and titration, g.	.0963	.0964	.2985	.2983	.2982

Summary

When simple precautions are observed, uranium can be determined accurately by weighing as U_3O_8 after precipitation as diammonium uranate, $(NH_4)_2U_2O_7$, or by titration with permanganate solution after passage through a Jones reductor.

In the gravimetric method it is recommended that macerated paper be used and that the precipitate be ignited in air. A simple method is given by which the uranium dioxide content of the U_3O_8 can be quickly checked by titration with permanganate after solution in hydrofluoric and sulfuric acids and addition of boric acid.

In the volumetric method it is recommended that the reduction be made in dil. sulfuric acid solution (1:20) at 20° to 25° and that the reduced solution be vigorously agitated by stirring or by a stream of pure air for five minutes before titration. It is shown that such exposure to the air insures complete oxidation of the over-reduced compound to the quadrivalent state and results in no further oxidation whatever.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, UNIVERSITY OF WISCONSIN]

A STUDY OF THE PHYSICAL PROPERTIES OF NITROMETHANE

BY JOHN WARREN WILLIAMS

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For many years the study of molecular rearrangements has received considerable attention from organic chemists. Various physical and chemical properties of certain substances made it evident that there were exceptions to the general rule of structural organic chemistry which states that every pure organic compound possesses a definite and fixed configuration which may be expressed by a single structural formula. For example, in the case of the so-called nitro compounds, Holleman,[1] Hantzsch and

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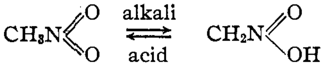
[1] Holleman, *Ber.*, **33**, 2913 (1900).

Schultze,[2] and Konowalow[3] were able to isolate isomeric modifications of certain aromatic nitromethanes. Studies of this sort raised the question as to the constitution of nitromethane itself, and it was shown by Hantzsch and his students that an equilibrium existed between tautomeric forms which may be represented as follows.



It was expected that nitromethane would show an irregularity in its specific heat-temperature curve, since it is believed that such an irregularity is evidence of the presence of more than one species of molecule.[4] The purpose of this paper is, then, to present the results of a study of its specific heat and other related properties. The properties are (1) specific heat, (2) vapor pressure, (3) density and (4) absorption spectrum.

Purification and Treatment

The nitromethane was obtained from the Eastman Kodak Company. It is probable that the principal impurity present in the liquid is water. In the studies to be presented the properties were determined on three distinct shipments of the material. A short summary of the treatments to which each shipment was subjected is given below. Each physical property was determined on each sample wherever necessary for the conclusions which were drawn.

Sample	Treatment	B. p., ° C. (760 mm.)	n^{22}_D
	SHIPMENT No. 1		
a	As received	98–101	1.38079
b	Dried with $CaCl_2$, fractionated	100.8–101.0	1.38061
c	b + 0.2% of water	....	1.38089
	SHIPMENT No. 2		
a	As received	98–101	1.38068
b	Dried with P_2O_5, fractionated	100.76–100.80	1.38048
c	b + 0.2% of water	....	.....
	SHIPMENT No. 3		
a	As received	98–101	1.38073
b	Dried with P_2O_5, fractionated	100.80–100.86	1.38056
c	b + 0.2% of water	....	1.38096
d	c, dried with $CaCl_2$, fractionated	100.85–101.05	1.38070

It will be noticed that the boiling points of the nitromethane dried with phosphorus pentoxide are more constant than those of the liquid dried with calcium chloride and are apparently slightly lower.

Experimental Part

The specific-heat determinations were carried out between 15° and 65°, the temperature intervals being between 3° and 6°. The results

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[2] Hantzsch and Schultze, *Ber.*, **29**, 699, 2251 (1896).

[3] Konowalow, *Ber.*, **29**, 2193 (1896).

[4] Williams and Daniels, THIS JOURNAL, **46**, 1569 (1924).

of these determinations are summarized in the four curves of Fig. 1. The method of procedure has been described in a previous communication.[5]

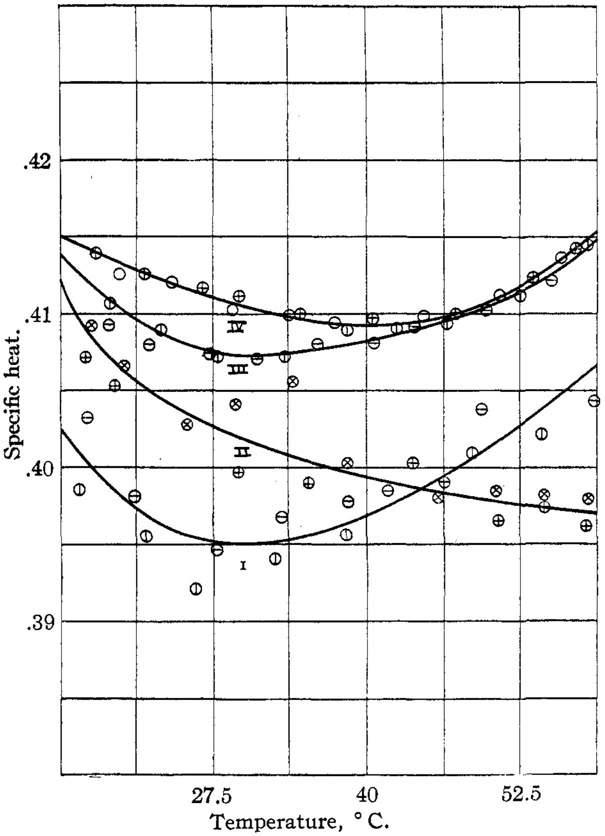

Fig. 1.—Specific heat of nitromethane. I. CH_3NO_2 dried with P_2O_5 ⊖ ⦶. II. CH_3NO_2 dried with $CaCl_2$ ⊕ ⊗. III. CH_3NO_2 as received ⊖ ⦶. IV. CH_3NO_2 + 0.20% H_2O ○ ⊕.

The empirical equations which give the specific heat at constant pressure (C_p) as a function of the temperature (centigrade) for the "purified" nitromethanes are given in Table I.

TABLE I

EMPIRICAL EQUATIONS

Nitromethane (dried with P_2O_5)	C_p (30–70°) $= 0.397_6 - 0.00033_8t + 0.0_581_5t^2$
Nitromethane (dried with $CaCl_2$)	C_p (15–70°) $= 0.420_9 - 0.00076_1t + 0.0_560_5t^2$

The vapor pressure of the nitromethane was determined for use in the Clapeyron equation, as well as to detect, if possible, any irregularity. The results of three series of determinations are summarized in Fig. 2,

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[5] Williams and Daniels, THIS JOURNAL, **46**, 903 (1924).

different characters representing different samples of nitromethane, as indicated. The method of Ramsay and Young[6] was used in these experiments.

The density of nitromethane was determined at frequent temperature intervals using a large (60 cc.) pycnometer. The values obtained may be given by the empirical equation, d_4^t (20–101°) = $1.1668 - 0.001358\,t - 0.0_655\,t^2$.

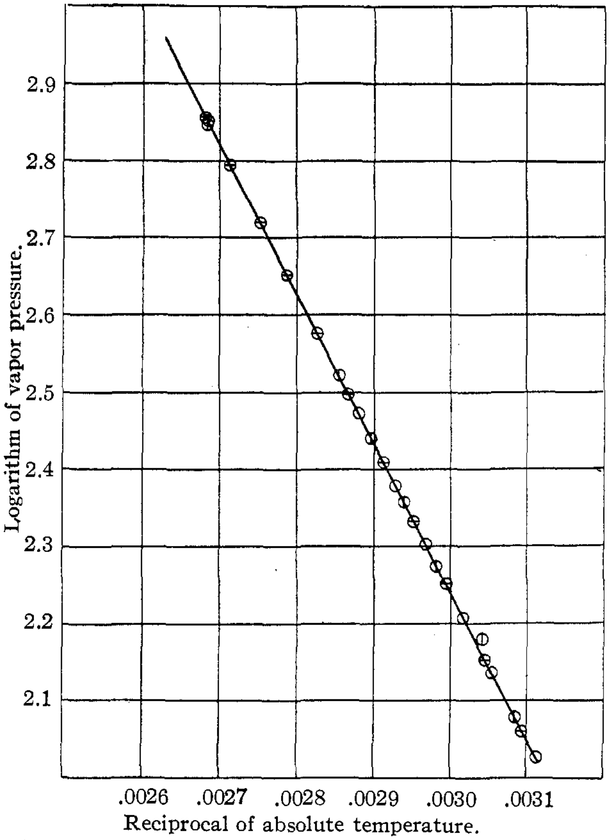

Fig. 2.—Vapor pressure of nitromethane. ○, CH_3NO_2 as received; ⊖, CH_3NO_2 dried with P_2O_5; ⦶, CH_3NO_2 dried with $CaCl_2$.

These density data are based upon weights in a vacuum. The agreement with data of other investigators is satisfactory, although Walden[7] reports a value which is slightly less (0.10%) over the range studied in this work. There is no indication of any irregularity in the temperature coefficient of density or of vapor pressure corresponding to the irregularities in the temperature coefficients of specific heat.

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[6] Young, *J. Chem. Soc.*, **59**, 911 (1891).

[7] Walden, *Z. physik. Chem.*, **65**, 139 (1909).

Finally, the absorption spectrum of nitromethane in the ultraviolet region was determined before and after drying. The instrument used was a quartz spectrograph. The absorption was practically complete at 3670 Å. Photographs taken using nitromethane as received, that which had been dried with phosphorus pentoxide, and that which had been dried with calcium chloride failed to show a detectable difference in the absorption.

Influence of Drying Agents

A detailed study of the effect of various drying agents on nitromethane would be exceedingly interesting, for the methods of drying found in the literature vary considerably. Phosphorus pentoxide, potassium carbonate, sodium sulfate, calcium chloride, copper sulfate and combinations of these substances have been used. Walden[7,8] in three papers published within three years used a different treatment in each, as follows: (1) sodium sulfate, then phosphorus pentoxide; (2) sodium sulfate; and (3) phosphorus pentoxide, then potassium carbonate. The constants reported by this investigator check very closely with those which are presented here for the nitromethane as it was obtained from the manufacturer and which presumably contained a slight amount of water. This will be evident from a study of Table II.

Table II

Comparison of Constants

Property	Nitromethane +0.20% of H_2O	Walden Ref. 7,8	Nitromethane From manufacturer	Nitromethane Dried with $CaCl_2$	Nitromethane Dried with P_2O_5
C_p (15–19°)	0.4145	0.4120	0.4100	0.4065	0.4010
n_D^{22}	1.38095	1.38090	1.38076	1.38065	1.38052
d_4^{25}	1.1312[a]	1.1308	.....	1.1320	1.1322

[a] Nitromethane +0.10% of H_2O.

These results tend to indicate that nitromethane gives slightly different physical constants when treated as described above.

Potassium carbonate, which gives an alkaline reaction in water solution, causes nitromethane to turn yellowish and gives it a strong odor. Nitromethane in water solution reacts acid toward litmus solution,[9] and it seems probable that the potassium salt of the acid form of nitromethane is formed when the potassium carbonate is added. For this reason the properties of nitromethane treated in this manner were not studied.

Calcium chloride could not be used to remove the last traces of water. It produces no visible effect, but the inner equilibrium must be disturbed, if the temperature-specific heat curve may be used as a criterion.

If phosphorus pentoxide is used a striking effect is noticed when slight amounts of water are present. A colloidal suspension is obtained which

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[8] Walden, *Z. physik. Chem.*, **58**, 490 (1907); **59**, 394 (1907).

[9] Hantzsch and Ley, *Ber.*, **39**, 3152 (1906).

does not settle. When the water content is reduced to within certain limits a gel is formed on standing, and there is apparently a relation between the amount of water present and the time required for the gel to set. Nitromethane of constant boiling point was distilled directly from phosphorus pentoxide over which it had stood for a week into several glass tubes which had been thoroughly cleaned and dried. To each tube was added a comparatively large amount of the phosphorus pentoxide and the tubes were sealed. The water content of each must have been very low, and it must have decreased in the order in which the samples were taken (that is, as the distillation continued). The material in the tubes set to a clear, solid gel in the same order, the first requiring one week and the third, one month Two more tubes were prepared as described above, and the open end was passed rapidly through a fine jet of escaping steam to introduce a trace of moisture. Then, as before, nitromethane was distilled into the tubes, phosphorus pentoxide added and the tubes sealed. The material in these tubes set to a clear, white gel in two days.

After the tubes were sealed, all were shaken to disperse the phosphorous pentoxide throughout the system, and it was noticed that the suspension formed was less stable in the nitromethane containing the smaller amounts of water, more stable in the liquid containing the intermediate amounts, and most stable in the liquid which had been saturated with water, as above.

A possible explanation of these effects is as follows. The phosphorus pentoxide is present in a finely divided condition and is surrounded by a protecting film of phosphoric acid which has been formed in the reaction with the water which is present in small amounts. Perhaps in this case the phosphoric acid—phosphorus pentoxide agglomerates are held in a definite and regular structure, with the nitromethane occupying the spaces within the gel structure.

From these experiments it seems probable that if the water concentration were reduced sufficiently the gel formation would be stopped. Additional evidence is obtained when nitromethane which has been freed from the gel by syneresis is shaken with the excess of phosphorus pentoxide in the tube before opening. The solid settles rapidly on standing, leaving an almost clear liquid. There are, then, apparently definite concentrations of water corresponding to the most rapid and positive formation of the gel, and above and below which gels do not form.

Discussion

Nitromethane shows an irregularity of some form in its specific heat-temperature curve regardless of the treatment to which it was subjected. When dried repeatedly with phosphorus pentoxide there is a distinct minimum at 30°. When dried with calcium chloride the specific heat *decreases* with temperature over the whole range studied (15–65°), and it is not until the temperature is raised almost to 70° that the curve begins to rise. With no treatment there is a minimum at 30°, and this minimum is shifted to 40° with the addition of 0.20% of water.

In the neighborhood of 20° the specific heat decreases rapidly with temperature, and at approximately the same rate in all four cases, indicating that the same process is taking place in the nitromethane no matter what its previous history has been, and it is not until 30° is reached that the curves show changes in slope. The specific-heat values for the purified liquids are irregular, but when traces of water are present, each point on the specific-heat curve falls nearly on a smooth curve. This may be regarded as confirmation of a similar effect of moisture in eliminating irregularities of points on the specific-heat curves of benzene and ethyl benzene, previously reported.[4]

The irregularities in the specific-heat curves for nitromethane which has been subjected to various treatments may be explained by a shift in the tautomeric equilibrium which has been discussed. When the temperature corresponding to the maximum in the curve has been passed (below 15°, but as yet undetermined) most of the molecules stable at the lower temperatures have been changed and the corresponding absorption of heat is less. According to the explanation of this phenomenon previously given,[4] a specific-heat curve with a negative slope will be obtained if this decrease in heat absorption per degree is greater than the natural increase in specific heat with temperature.

It is of interest to note that the ratio of the molecular heat to the molecular volume for nitromethane is high over the range of temperature investigated, indicating that part of the observed specific heat is due to heat absorbed in shifting the equilibrium. It has a value between 0.45 and 0.50, while that of a normal liquid is approximately 0.35. This ratio apparently reaches a minimum between the temperatures 30° and 50° in the case of the nitromethane purified with phosphorus pentoxide, and decreases steadily in the case of the nitromethane treated with calcium chloride, until a temperature of 65° is reached. It is the only liquid of some 20 which have been carefully studied in which the ratio was found to decrease.

Vapor-pressure and density curves do not exhibit irregularities corresponding to the irregularities in the specific-heat curves. The density of nitromethane at its boiling point was determined by Brühl[10] and found to be 1.0236. A calculation based on the equation presented on p. 2647 gives a value 1.0242 for this temperature, showing that there is no irregularity that can be detected over the whole range of temperature from 25° to 100°.

[10] Brühl, *Z. physik. Chem.*, **16**, 215 (1895).

The latent heat of evaporation of nitromethane was calculated from the vapor-pressure data using the differential form of the Clapeyron equation. The volume of 1 g. of the vapor was calculated from the vapor density of nitromethane. The vapor density was determined, using a Dumas bulb, at 108.7° and found to be 0.001972. The specific volume of the vapor was calculated at this temperature and corrected to 100° (the temperature at which the latent heat of the nitromethane was determined) by means of the perfect gas laws. The specific volume of the liquid was calculated from the value of the density at the boiling point.

The value of dP/dT for use in the equation was determined by multiplying that of $d \log P/dT$ by the pressure and suitable conversion factors. The value of $d \log P/dT$ was obtained from the curve showing the relation between the logarithms of the vapor pressures against the reciprocals of the absolute temperatures (Fig. 2). This relation may be expressed by the equation, $\log P = -1928/T + 8.033$.

Making the substitutions, the latent heat obtained is 137.1 as compared to the experimentally determined value of 134.9.[11]

The possibility of an abnormal boiling point when nitromethane is subjected to intensive drying may be mentioned. Since phosphorus pentoxide is dispersed as a colloid in the liquid it was thought that rapid and efficient drying should result, but the formation of a gel complicated the situation. It is probable that the phosphorus pentoxide is present in a finely divided condition, and is surrounded by a protecting film of phosphoric acid which has been formed in the reaction with the small amount of water which is present. Then the phosphorus pentoxide would no longer be effective in the drying process.

It is believed, however, that the water may be so reduced that the gel will not form, and if this liquid be further dried in tubes similar to those used by Baker[12] and by Smits[13] it will show that nitromethane behaves as a mixture. Several preliminary and less refined experiments have shown slight increases in the temperature of the boiling point (0.5° over a period of six months) and it is proposed to continue this study along with that of the gel formation.

Grateful acknowledgment is hereby made to Professor Farrington Daniels for many helpful suggestions during the course of the work.

Summary

1. Certain physical properties of nitromethane (which has been subjected to different drying treatments), namely, specific heat, vapor pressure, density and ultraviolet absorption, have been determined.

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[11] Mathews, forthcoming publication.

[12] Baker, *J. Chem. Soc.*, **101**, 2339 (1912).

[13] Smits, *ibid.*, **125**, 1068 (1924).

2. The specific heat-temperature curves of the various nitromethanes showed distinct irregularities, which indicate the presence of several species of molecules in the liquid.

3. Measurements of vapor pressure and density failed to show corresponding irregularities.

4. A nitromethane gel with phosphorus pentoxide and a trace of water is described.

5. The probability of an abnormal boiling point for nitromethane which has been subjected to intensive drying is discussed.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 72]

ON THE DERIVATION OF THE EQUATION FOR THE EFFECT OF TEMPERATURE ON REACTION RATE

BY RICHARD C. TOLMAN

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In order to account for the large temperature coefficient of the rate of ordinary chemical reactions, it seems impossible to escape the conclusion of Arrhenius[1] that the molecules which actually enter into the reaction must be in an activated form containing considerably more energy than the normal molecule.[2] In accordance with this view of Arrhenius, it has been customary to use the following equations to express the rates of first order unimolecular and second order bimolecular reactions, respectively, as functions of the temperature

$$-\mathrm{d}C/\mathrm{d}t = kC = k'\, e^{-E/RT}\, C \tag{1}$$

$$-\mathrm{d}C/\mathrm{d}t = kCC' = k'T^{1/2}\, e^{-[(E+E')/RT]}\, CC' \tag{2}$$

where E or $(E + E')$ are the energy contents per mole of the activated molecules entering into the reaction.[3]

Since the older derivations of these equations have involved special assumptions, a somewhat more elaborate analysis of the justification for the equations will not be out of place. We shall find that the magnitudes

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[1] Arrhenius, *Z. physik. Chem.*, **4**, 226 (1889).

[2] The transition of the molecule from the normal to the activated form may be merely a change to a higher quantum state or other tautomer of high energy content or may involve dissociation or other change which is usually regarded as chemical. In the sense of the Arrhenius formulation, the "residual molecules" of Rice, Fryling and Wesolowski [THIS JOURNAL, **46**, 2405 (1924)] would often seem to be one special kind of activated molecules.

[3] The actual equation proposed by Arrhenius had for any order of reaction the form $\frac{\mathrm{d} \log k}{\mathrm{d}\, T} = \frac{E}{RT^2}$ where E is the total energy of activation. The introduction of the term $T^{1/2}$, however, in Equation 2 for bimolecular reactions is customary, since the number of collisions between molecules is proportional to this power of the temperature.