The average radius of an air molecule was taken as 1.54×10^{-8} cm.[6] and is the second term in the parentheses on the left-hand side of the equation.

The radii so calculated are listed in Table II, together with molecular radii calculated from the densities of the corresponding liquids on the assumption that the molecule occupies a volume equal to that of a cube with a side whose length equals the diameter of the molecule. The agreement between the two methods is excellent.

TABLE II

MOLECULAR RADII

Vapor	From diffusion coefficient, in Å.	From liquid density, in Å.
CCl_3NO_2	2.78	2.75
$COCl_2$	2.42	2.45
CNCl	2.31	2.19
HCN	2.03	2.00

DEPARTMENT OF CHEMISTRY
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RECEIVED MAY 28, 1947

Dielectric Studies. VIII. Dipole Moments of Solvents in Nonpolar Solvents of Unknown Molecular Weights[1]

BY NORMAN C. C. LI,[2] C. V. AN AND W. H. WU

In a recent paper Li and Chu[3] reported the dipole moment of acetonitrile in three solvents of unknown and variable molecular weights, namely, gasoline, kerosene and petroleum ether. It was shown that in determining the molar polarization at infinite dilution, graphical extrapolation is not necessary and the molecular weight of the non-polar solvent used need not be known, if the dielectric constant and density of dilute solutions are linear functions of weight fractions of the solute. In this study we report dipole moment values of two polar solvents, namely, acetone and chloroform in two different samples of gasoline of different physical properties.

Acetone of tested purity was refluxed over potassium permanganate, placed over anhydrous calcium chloride and subsequently carefully fractionated. The fraction boiling between 56 and 56.5° was taken, its refractive index being $n^{25}\text{D}$ 1.3567. Chloroform of U.S.P. grade was purified from alcohol by one thorough extraction with 9 *M* sulfuric acid followed by six extractions with water. The product was dried over freshly-fused calcium chloride and distilled, b. p. 61–61.5°. Gasoline, colorless grade, was used without further purification. The samples came from different sources with different refractive indices: sample A, $n^{25}\text{D}$ 1.4242; sample B, $n^{25}\text{D}$ 1.4287.

The apparatus for determinations of dielectric constant, density and refractive index have been described by Li and Chu.[2]

The results of the experimental work are presented in Tables I and II. The dielectric constant data are accurate to about 0.1%.

TABLE I

Acetone in gasoline (sample A) 25°			Chloroform in gasoline (sample B) 15°		
W_2	E	d	W_2	E	d
0.0000	2.032	0.7452	0.0000	2.051	0.7525
.0182	2.253	.7461	.0384	2.097	.7708
.0330	2.452	.7466	.0582	2.119	.7795
.0541	2.700	.7475	.0719	2.136	.7856
.0615	2.778	.7479	.0933	2.163	.7943
.0861	3.111	.7489			

In Table I the headings W_2, E, d are the weight fraction of solute, dielectric constant and density, respectively.

TABLE II

CONSTANTS OF THE GASOLINE

	Sample A	Sample B
$C(= 3/d_1(E_1 + 2)^2)$	0.2476	0.2430
$p_1 = (E_1 - 1)/(E_1 + 2)d_1$	.3435	.3447

Subscript 1 refers to solvent.

Data in Table I indicate that dielectric constant and density are linear functions of weight fractions W_2, and therefore the method and formulas described by Li and Chu[2] can be used and a knowledge of the molecular weight of the non-polar solvent is not necessary. The formulas used are

$$P_{2(\infty)} = [p_1(1 - b) + CaE_1]M_2 \qquad (1)$$

$$\mu = 0.01273 \times 10^{-18} \sqrt{(P_{2(\infty)} - P_{2\text{D}})T} \qquad (2)$$

where $P_{2(\infty)}$ is the molar polarizarion of the solvents at infinite dilution, p_1 is the specific polarization of the solvent $\left(\frac{E_1 - 1}{E_1 + 2}\frac{1}{d_1}\right)$, a and b are the dielectric constant and density coefficients in the equations $E = E_1(1 + aW_2)$ and $d = d_1(1 + bW_2)$, respectively, $C = 3/d_1(E_1 + 2)^2$, M_2 is the molecular weight of the solute. The dipole moments for acetone and chloroform in gasoline are calculated to be 2.8 and 1.16×10^{-18}, respectively. These values are in good agreement with the values given in the literature, namely, 2.72 and 1.15×10^{-18}, respectively, when solvents of known and definite molecular weights were used.

For the past four years the senior author of this paper and his students have examined over ten different compounds dissolved in non-polar solvents of unknown molecular weights. In each case they have found that the dielectric constant and density of the mixture are linear functions of weight fractions for solutions whose concentrations are less than 8%, and that the values of the dipole moments thus obtained are correct. Many different samples of gasoline, kerosene and petroleum

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(1) Presented before the Division of Physical and Inorganic Chemistry of the American Chemical Society, Atlantic City Meeting, April, 1947.

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(3) Li and Chu, THIS JOURNAL, **69**, 558 (1947).

ether have been used as solvents without any purification, and the results are the same.

DEPARTMENT OF CHEMISTRY
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RECEIVED MAY 15, 1947

Thermal Decomposition of Ammonium Nitrate

BY J. T. KUMMER

Recent interest in the decomposition of ammonium nitrate seems to make it worthwhile to call attention to an observation made recently during the preparation of a $N^{14}N^{14}$, $N^{14}N^{15}$, $N^{15}N^{15}$ mixture from a sample of NH_4NO_3 (Eastman Kodak Co.) in which the ammonium group contained 62 atom per cent. N^{15} and 38 atom per cent N^{14} and the nitrate group contained the 0.38% N^{15} of normal nitrogen. This NH_4NO_3 was decomposed, after it had melted, at 290° to give nitrous oxide. The nitrous oxide was then permitted to react quantitatively with a reduced iron catalyst at room temperature to give nitrogen and iron oxide. The nitrogen, when analyzed by a mass spectroscope, was found to contain 0.35% $N^{15}N^{15}$. If the ammonium nitrate molecule decomposed by the reaction of the ammonium group with the nitrate group, the percentage of $N^{15}N^{15}$ would be 0.24; whereas if all the nitrogen atoms present in the ammonium nitrate combined at random, the percentage of $N^{15}N^{15}$ would be 9.6. These results show that the decomposition of the ammonium nitrate to give N_2O proceeds practically entirely by a bond formation between the two nitrogen atoms of the two different groups present, and not by the interaction of similar groups.

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RECEIVED AUGUST 18, 1947

An Extension of the Scope of the Hammick Reaction

BY KURT MISLOW

The synthesis of α-pyridylcarbinols by the decarboxylation of picolinic acid in an excess of aldehyde or ketone was first reported by Hammick and co-workers.[1,2] These authors, after an apparently exhaustive investigation of a large number of decarboxylating acids, reported that ". . . the decarboxylation of pyridine and quinoline acids other than those containing the carboxyl group α to the nitrogen atom yielded no products of interaction with aldehydes and ketones."[2]

The similarity of the reactivity of the α- and γ-positions on the pyridine ring suggested, however, that this reaction might not necessarily be restricted to picolinic, quinaldinic and isoquinaldinic acids, but that it might be extended to include acids such as isonicotinic acid.

When isonicotinic acid was decarboxylated in boiling benzophenone, a small yield of diphenyl-γ-pyridylcarbinol was indeed realized. Benzophenone was selected as the solvent reagent because it had been shown[2] to react with decarboxylating picolinic acid and because its boiling point roughly coincides with the decarboxylating temperature of isonicotinic acid.

This result indicates that the Hammick reaction is of greater generality than has hithertofore been assumed.

Experimental[3]

A mixture of 19.8 g. (0.16 mole) of recrystallized isonicotinic acid and 250 g. (1.37 mole) of benzophenone was refluxed for nine and one-half hours, an air condenser being employed. A sealed-in plunger arrangement helped to scrape sublimed crystals of isonicotinic acid back into the reaction mixture. After five hours, 3600 ml. of carbon dioxide had been evolved (90% of the theory), and in the subsequent four and one-half hours, only 50 ml. more of the gas was evolved. The dark brown solution was allowed to cool to room temperature, diluted with 500 ml. of benzene and extracted with 2.5 *N* hydrochloric acid (more concentrated acid precipitates a tar, which redissolves on dilution). The acid extracts were made alkaline and extracted with benzene. The solid A at the interface was removed by centrifugation and the benzene layer was evaporated to dryness. The partially crystalline residue was freed of oil by washing with acetone, leaving 0.85 g. of crystals, m. p. 192–232°; recrystallization of A from benzene–pyridine gave an additional 0.6 g. of tan prisms, m. p. 205–232°. The total yield of crude carbinol thus amounted to 3.5%. Further recrystallization from benzene–pyridine afforded colorless microscopic prisms, m. p. 237–238°.

Anal. Calcd. for $C_{18}H_{15}ON$: C, 82.73; H, 5.79; N, 5.36. Found: C, 82.94; H, 5.79; N, 5.09.

Tschitschibabin and Benewolenskaja,[4] who prepared this compound by the action of phenylmagnesium bromide on phenyl-γ-pyridylketone, report a melting point of 235°.

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[1] Dyson and Hammick, *J. Chem. Soc.*, 1724 (1937).

[2] Ashworth, Daffern and Hammick, *ibid.*, 809 (1939).

[3] All melting points are corrected; microanalysis by Dr. G. Oppenheimer and Mr. G. A. Swinehart.

[4] Tschitschibabin and Benewolenskaja, *Ber.*, **61**, 547 (1928).

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RECEIVED MAY 31, 1947

Correlation of Surface Area and Dehydrogenation Activity for a Chromia–Alumina Catalyst

BY J. R. OWEN

In connection with dehydrogenation of normal butane at Plains Butadiene Plant, which is operated by Phillips Petroleum Company for Reconstruction Finance Corporation—Office of Rubber Reserve, a laboratory study was made of dehydrogenation activity and surface area of several samples of chromia–alumina catalyst A[1] that were used in the plant.

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[1] G. H. Hanson and H. L. Hays, *Chem. Eng. Progress*, to be published.