The Preparation and Physical Properties of Pure Pyridine and Some Methyl Homologues.

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The methods used in the preparation from commercially available material of samples of pyridine, α-, β-, and γ-picoline, and 2 : 6-lutidine of purity greater than 99·7 moles % are described. The purities of the samples have been established by freezing-point measurements, and the freezing points, cryoscopic constants, and latent heats of fusion of the 100% pure bases have been computed. The normal boiling points have been measured with a standard deviation of less than ±0·005°. The pressure coefficients of the boiling points and the latent heats of vaporization are also placed on record. The densities of anhydrous base samples at 20° and at 30° have been measured and the coefficients of cubical expansion at 25° have been derived. The refractive indices for the *C*, D_1, *e*, and *F* lines of the anhydrous bases at 20° have been found and fitted to a modified Hartmann equation : $n = n_\infty + C/(\lambda - \lambda^*)^{1\cdot6}$. The molar refractivities have also been calculated. The infra-red spectra of the highly purified base samples in the liquid and vapour states have been measured for the wave-length range 2—15 μ.

PYRIDINE and its methyl homologues would offer a wide scope for studies of the relation between structure and properties but for the inaccessibility of many members of the series. The technical interest which, however, now attaches to certain of the homologues prompted an undertaking of various physico-chemical measurements, for which there would ultimately be required substantial quantities of all the homologues. Some of the physico-chemical measurements made in this laboratory on the more readily accessible bases have already been placed on record : vapour pressures, Herington and Martin, *Trans. Faraday Soc.*, 1953, **49**, 154 ; solubilities in water and in D_2O, Andon and Cox, *J.*, 1952, 4601, Cox, *ibid.*, p. 4606 ; ultra-violet absorption spectra and dissociation constants, Herington, *Discuss. Faraday Soc.*, 1950, **9**, 26 ; and heats of formation, Cox, Challoner, and Meetham, *J.*, 1954, 265 ; and others are in progress. Since one of the main purposes in this programme was the critical assessment of existing physico-chemical data, it is clear that the final purification and the quantitative estimation of residual impurity are crucial. It is, indeed, particularly true that discrepant and erroneous statements on the physical and chemical properties of individual bases in this series have been the result of observations on impure materials. This paper therefore presents work on the purification of pyridine, the three isomeric picolines, and 2 : 6-lutidine, and on the measurement of some salient physical properties.

These five bases, separated from coal tar or crude benzole fractions, are available in commercial grades of various qualities. The purity of the best of these, " Pyridine A.R.," is above 99% ; that of the others such as β- or γ-picoline may be as low as 95%. The standard of purity we set ourselves, *ca.* 99·9 moles % as deduced from the freezing- or melting-point curve, proved very difficult to achieve, even from the best grades of starting material, because (*a*) small amounts of pyrrole derivatives, sulphur compounds, hydrocarbons, and phenols may be present, (*b*) some homologues, *e.g.*, β- and γ-picoline, have very similar boiling points, and (*c*) the bases are hygroscopic. Thus it was first necessary to remove non-basic contaminants. Further treatment consisted of two or all of the processes, distillation (fractional or azeotropic), fractional crystallization from a melt, and crystallization of a suitable complex compound.

The following properties have now been measured or computed, collated with published values, and placed on record : freezing points, latent heats of fusion, and cryoscopic constants (Table 2) ; boiling points, pressure coefficients of boiling point, and latent heats of vaporization (Table 3) ; densities at 20° and at 30°, and coefficients of cubical expansion at 25° (Table 4) ; refractive indices for the *C*, D_1, *e*, and *F* lines at 20°, and molar refractivities for the D_1 line (Figs. 2—6, Table 5) ; and infra-red absorption spectra (2—15 μ) for the liquids (Table 7). They include the properties likely to be of greatest use in the characterization of specimens of these bases and in setting up analytical techniques. The thermal data are also of interest to chemical engineers.

EXPERIMENTAL

Purification of Individual Bases.—Pyridine. This base has no homologues of similar b. p., so fractional distillation is effective for preliminary purification (Heap, Jones, and Speakman, *J. Amer. Chem. Soc.*, 1921, **43**, 1936; Wilkie and Shaw, *J. Soc. Chem. Ind.*, 1927, **46**, 469T; Carignan and Kraus, *J. Amer. Chem. Soc.*, 1949, **71**, 2983). But we found that even repeated distillation, in a column of 50-plate efficiency, of commercial pyridine of the best quality did not suffice.

Other processes of purification which have been used are: crystallization of the zinc chloride complex (Carignan and Kraus, *loc. cit.*); crystallization of the perchlorate (Arndt and Nachtwey, *Ber.*, 1926, **59**, 448) and of the hydrogen oxalate (Rozhdestvenskii, Pukirev, and Maslova, *Trans. Inst. Pure Chem. Reagents, U.S.S.R.*, 1935, No. **14**, p. 58); and combination of fractional freezing with distillation (Leis and Curran, *J. Amer. Chem. Soc.*, 1945, **67**, 79). In some of these cases the products were dried, but there is no record of any previous attempt to estimate the residual moisture or to evaluate the total molar percentage of residual impurities from freezing-point behaviour.

To remove non-basic, particularly sulphur-containing, contaminants (Coulson and Ditcham, *J. Appl. Chem.*, 1952, **2**, 236) steam was passed through a boiling solution of the base in 1·2 equivs. of 22·6% sulphuric acid until about 10% of the pyridine had been carried off along with contaminating substances. Base was then liberated by an excess of concentrated aqueous sodium hydroxide, separated, and dried over solid sodium hydroxide. Fractional distillation through a 50-plate Stedman gauze-packed column (reflux ratio 50 : 1) gave a fraction of b. p. 93·7—94·0°/400 mm. and purity 99·5 moles % (f.-p. curve). The main residual impurity was water, it being difficult to avoid atmospheric contamination. Infra-red spectroscopy (Coulson, Hales, and Herington, *J.*, 1951, 2125) was capable of detecting 0·002% by vol. (0·01 mole %) of water in pyridine, and up to 0·5 mole % of water was found in samples obtained as above. The best specimen had a purity of 99·85 ± 0·03 moles % (f.-p. curve) and was obtained by subjecting the 99·5% sample to fractional freezing and then simple distillation to remove water and tap-grease. By the use of a Dewar vessel, the exhaustion of which could be varied at will, the base was cooled at a controlled rate to a temperature just below the f. p. and allowed to crystallize slowly until about one-tenth remained liquid. The liquid was then drawn off and the crystals were melted and the process was repeated a number of times, all in a closed apparatus. The purified base was then transferred to a thoroughly dry all-glass still and about 25% was slowly distilled off. Distillation of the residue gave the best specimen. A specimen of 99·87 moles % purity was obtained by adding about 10% of pure benzene (cf. Berg, Harrison, and Montgomery, *Ind. Eng. Chem.*, 1945, **37**, 585) to the 99·5% material and fractionally distilling it through a 50-plate Stedman column, a forecut containing water and benzene being taken off and a bulk fraction of b. p. 93·7—94·0°/400 mm. being collected. The latter, although very dry, contained benzene and when diluted with a large volume of water became cloudy: it was therefore not used for the physical measurements.

α-Picoline. α-Picoline also can be purified considerably by fractional distillation (Wilkie and Shaw, *J. Soc. Chem. Ind.*, 1927, **46**, 469T; Hoffman and VanderWerf, *J. Amer. Chem. Soc.*, 1946, **68**, 997; Freiser and Glowacki, *ibid.*, 1948, **70**, 2575). When a commercial specimen of "pure" α-picoline in aqueous sulphuric acid was treated with steam as above, a small amount of a mixture of xylenes (chiefly *m*- and *p*-) was found in the condensate. The remaining purification and the drying were the same as for pyridine, and the best specimen had 99·87 ± 0·01 moles % purity (f.-p. curve). When α-picoline is supercooled it crystallizes in an unstable form melting about 0·13° below the stable form, and care must be taken to seed the liquid with the stable form when the f.-p.–time curve is plotted for purity determination.

The only previous determination of the purity of a purified α-picoline (99·85 moles %) is that of Freiser and Glowacki (*loc. cit.*) who also noted the two crystalline forms. The residual impurity in their specimen, as in ours, was mainly water (Coulson, Hales, and Herington, *loc. cit.*).

β-Picoline. The main source of difficulty in the preparation of β-picoline is its natural association, in coal tar, with γ-picoline and 2 : 6-lutidine which have b. p.s extremely close to, and on either side of, that of β-picoline. The separation and purification of these compounds were studied by Coulson and Jones (*J. Soc. Chem. Ind.*, 1946, **65**, 169; B.P. 585,108, 598,036, 602,273). Many methods of separation have been suggested more recently, but, although they have all been used to prepare concentrates, very few have been applied to the preparation of the three bases in pure states (see, however, Hoffman and VanderWerf, *J. Amer. Chem. Soc.*, 1946, **68**, 997; Brown and Barbaras, *ibid.*, 1947, **69**, 1137; Johnson, *J.*, 1947, 1626; Angyal, *J. Proc. Austral. Chem. Inst.*, 1947, **14**, 12; Riethof, Richards, Savitt, and Othmer, *Ind. Eng. Chem. Anal.*, 1946, **18**, 458 ; Glowacki, Winans, and Koppers Co., U.S.P. 2,402,158). We did not find the method of Riethof, Richards, Savitt, and Othmer, (*loc. cit.*; reaction with acetic and phthalic anhydride) to be as specific as claimed, and we were not able to prepare β-picoline, by this or any other method, which did not react to some extent with phthalic and acetic anhydrides. The purity of a specimen, originally 96%, was not raised beyond 99% by exhaustive treatment with the anhydrides.

We found that the most convenient separation of pure β-picoline from commercial coal-tar materials involved the following steps. After removal of non-basic contaminants, as for pyridine, cruder specimens (30—90% of β-picoline) were treated with urea for removal of 2 : 6-lutidine. β-Picoline so obtained (90% or purer) was then azeotropically fractionated with acetic acid (Coulson and Jones, *loc. cit.*). The base recovered from the azeotrope, b. p. 114·5°/212 mm., by treatment with excess of 30% aqueous sodium hydroxide, was dried over solid sodium hydroxide and then by very slowly distilling off a small amount, in which water was removed, until the b. p. was constant. This base had 96% purity and was suitable for fractional freezing. It was then kept at such a temperature that at least 24 hr. were required, after seeding, before about 90—95% was frozen. The liquid was poured off, the crystals were melted, and the process was repeated 5—6 times or until an examination of the f.-p. curve showed that the required purity had been reached. The best sample of β-picoline so secured was dried by slowly distilling off a forecut, and had 99·97 ± 0·02 moles % purity.

γ-Picoline. Pure γ-picoline, from commercially available specimens (90—95%) or from a β-picoline cut (*ca.* 30%), was prepared similarly to the β-isomeride. Non-basic material was removed, then 2 : 6-lutidine, if necessary, through the urea complex. Next the purity was raised to 98% by azeotropic fractionation, the acetic acid azeotrope being collected at 116·5—117°/212 mm., and finally a best sample (99·88 ± 0·02 moles %) was secured by slow fractional freezing at temperatures close to the m. p. of the pure base.

2 : 6-*Lutidine.* Pure 2 : 6-lutidine was separated from three sources, two being commercial specimens of the base, and the third a typical " β-picoline cut " of tar bases, from which pure β- and γ-picolines were also separated. In each case non-basic contaminants were removed first. It was not difficult by azeotropic fractionation (Coulson and Jones, *loc. cit.*) to raise the purity of 2 : 6-lutidine from all these sources to 95 moles %, but fractional freezing did not then prove economical. Crystallisation of the urea complex (Riethof and Pittsburgh Coke and Iron Co., B.P. 592,384; U.S.P. 2,383,016, 2,295,606) was very effective either for the concentration of 2 : 6-lutidine or for raising the purity of 90—95% material to 99 moles %, beyond which fractional freezing is preferable.

The best procedure was as follows. To a mixture of 450 g. of water and 527 g. of urea there was added 470 g. of commercial 2 : 6-lutidine or an equivalent amount of a picoline cut. After being heated under reflux until two liquid layers were obtained and no solid remained undissolved, the mixture was cooled, with stirring, whereupon the complex crystallized. It was filtered off and added to 450 g. of water, and the whole was warmed until no solid remained, then stirred and cooled to induce crystallization. After a second recrystallization from 450 g. of water, the purified complex was boiled for 6 hr. under reflux with sodium hydroxide (500 g.) in water (1150 g.). When the liquid was cooled, regenerated 2 : 6-lutidine separated. It was removed, dried (NaOH), and distilled. The yield was 78% of material of purity *ca.* 99 moles %. Base recovered from the filtrates was worked up for β- and γ-picolines.

The best sample of 2 : 6-lutidine was obtained by slow fractional freezing of the 99% material, followed by a final distillation. Its purity was 99·89 ± 0·01 moles %.

Examination of Purified Bases for Particular Impurities.—Pyrrole. None of the five pure bases, in the form of its hydrochloride, gave a detectable colour with *p*-dimethylaminobenzaldehyde; each therefore contains less than 1 p.p.m. (0·0001 mole %) of pyrrole or pyrrole homologue, which is the limit of the sensitivity of this test in the presence of these pyridine bases.

Sulphur. The sulphur contents, determined by combustion, were all less than 0·003 mole %.

Physico-chemical Measurements.—Freezing points, latent heats of fusion, cryoscopic constants, *and the quantitative estimation of purity.* The cryoscopic technique was determined by the extreme hygroscopicity, the need to add known amounts of impurity (as cryoscopic constants were unknown), and the need for economy of material. A 20-ml. sample was placed in the apparatus described by Herington and Handley (*J.*, 1950, 199), a thermocouple being used in place of the thermistor. One junction was placed in a triple-point water cell and the measurements of e.m.f. were made with a Tinsley three-dial vernier potentiometer. Readings were obtained on the last dial to 1 µv and values to the nearest 0·05 µv were obtained by interpolation from the galvanometer deflections.

A very general method of calculating the purity and the freezing-point constants of a material from the behaviour of samples during freezing is discussed by Schwab and Wichers (" Temperature. Its Measurement and Control in Science and Industry," Reinhold Publ. Corp., New York, 1941, p. 256), and a modified form of this was employed. A great advantage is that the rate of crystallization need not be assumed to remain constant throughout the freezing period. One assumes merely that the same fraction of solid is formed at equal fractions of the total freezing time in experiments with and without added impurity, and this can be checked by repeating the experiment after the addition of a second portion of impurity.

The technique was therefore as follows. A curve of temperature against time was obtained for a purified sample of base and the experiment was then repeated under the same conditions after the addition of a known amount of impurity. *iso*Octane was employed as impurity because it was thought that this would not form mixed crystals with the base; this was confirmed for pyridine, whose latent heat of fusion calculated from the results obtained by the use of *iso*octane agreed with the best published values. The data obtainable from these two curves alone are sufficient to calculate the cryoscopic constant, the purity of the sample, and the f. p. of the 100% pure base, but the experiment was repeated after the addition of a further quantity of *iso*octane. Table 1 summarises a typical experiment. The time for complete freezing was determined by graphical analysis (see, for example, Stull, *Ind. Eng. Chem. Anal.*, 1946, **18**, 234), and the initial f. p. of the actual sample (t_f) was also estimated from such a plot. The values of y being proportional to x_1, the depression θ (°c) of the initial f. p. produced by 1 mole % of impurity, is readily calculated, the calibration of the thermocouple being used to convert µv into °c. From the value of θ so obtained and the f. p. of the 100% material (see below), the cryoscopic constant, K_f, and the latent heat of fusion can be calculated. Each value of Δt (µv) corresponds to the difference between the initial f. p. and the freezing temperature at a time equal to half that required for complete freezing. The changes in Δt produced by added impurity (column 5, Table 1) are proportional to the amounts of added impurity but corresponding values in columns 3 and 5 are not equal; it follows that not exactly half the charge is frozen at a time equal to half that required for complete freezing, and hence that the mathematical analysis of the curves advanced by Rossini *et al.* (*J. Res. Nat. Bur. Stand.*, 1941, **26**, 591; 1944, **32**, 197) cannot be employed with the present results. In particular the thermocouple e.m.f. corresponding to the f. p. of the 100% pure material cannot be obtained by simply subtracting the value (1·7) given for the original sample from that in column 2. When the conditions shown in Table 1 exist, the number of microvolts which must be subtracted from the e.m.f. corresponding to the initial f. p. of the original sample to obtain the e.m.f. corresponding to the f. p. of the 100% pure pyridine base, is given by $y\Delta t_1/(\Delta t_2 - \Delta t_1)$, where Δt_1 and Δt_2 refer respectively to observations before and after addition of impurity. For a material (*e.g.*, γ-picoline) which freezes above +0·010° the value of $y\Delta t_1/(\Delta t_2 - \Delta t_1)$ must be added instead of subtracted, to yield the thermocouple e.m.f. corresponding to the f. p. of the 100% pure material. The molar percentage (x) of impurity in the original sample is given by the expression $x_1\Delta t_1/(\Delta t_2 - \Delta t_1)$ where x_1 is the molar percentage of added impurity. The initial f. p. of the actual sample expressed on the International Temperature Scale (t_f) was obtained by calibrating the thermocouple directly after use against a platinum resistance thermometer at very nearly the temperature under investigation.

TABLE 1. *Pyridine. Temperatures are given in terms of the e.m.f.* (µv) *of the thermocouple.*

	Initial f. p. (t_f)	Depression (y) by impurity	Δt	Change in Δt produced by impurity
Original sample	1444·0	—	1·7°	
After the addition of 0·318 mole % of *iso*octane (x_1 = 0·318)	1450·05	6·05	3·5	1·8°
After the addition of 0·605 mole % of *iso*octane (x_1 = 0·605)	1456·45	12·45	5·65	3·95

Curves were determined twice for each value of x_1. The derived quantities θ, x, and $t_{f,0}$ (the f. p. of 100% pure material) were calculated from the mean values of y, Δt_1, and Δt_2. The standard deviations of θ, x, and $t_{f,0}$ were also calculated, the errors arising from uncertainties in x_1 being neglected, *i.e.* from $\sigma_\theta^2 = (\sigma_{t,f}^2 + \sigma_{t,2}^2)/x_1^2$, where $\sigma_{t,f}$ and $\sigma_{t,2}$ are the standard deviations of the mean initial f. p. of the original sample, and of the mean initial f. p. after the addition of x_1 moles % of impurity. The separate values of θ so obtained were then treated as if they were independent determinations and were combined to give a grand mean and standard deviation, each value of θ being weighted by the appropriate σ_θ^{-2} term. The final results so obtained are listed in Table 2.

TABLE 2. *Freezing constants for pyridine, α-, β-, and γ-picoline, and 2 : 6-lutidine.*

	Purity (100 − x) moles %	Depression (θ) produced by 1 mole % of impurity	Depression (K_f) for 1 mole of impurity in 1000 g.	Latent heat of fusion (l_f, cal./g.)	F. p. of sample (t_f)	F. p. for 100% purity ($t_{f,0}$)
Pyridine	99·73	0·607°	4·75°	22·4	−41·71°	−41·55°
	±0·03	±0·017°	±0·13°	±0·6	±0·04°	±0·05°
α-Picoline ...	99·83	0·365	3·36	25·2	−66·81	−66·74
	±0·01	±0·060	±0·55	±4·1	±0·04	±0·04
β-Picoline ...	99·89	0·529	4·88	26·5	−18·25	−18·20
	±0·02	±0·015	±0·14	±0·8	±0·04	±0·04
γ-Picoline ...	99·88	0·557	5·13	29·7	+3·58	+3·65
	±0·02	±0·029	±0·27	±1·7	±0·04	±0·04
2 : 6-Lutidine	99·89	0·596	6·32	22·4	−6·16	−6·10
	±0·01	±0·026	±0·28	±1·0	±0·04	±0·04

The cryoscopic constants, K_f, were then calculated from these grand mean values of θ, and the standard deviations, $\sigma_{K,f}$, of K_f were derived from the expression $K_f\sigma_\theta/\theta$. The latent heats of fusion were obtained by means of the expression $\boldsymbol{R}T_{f,0}^2/1000K_f$, where $T_{f,0}$ is $t_{f,0}$ converted into degrees Kelvin, and their standard deviations, $\sigma_{l,f}$, were computed by the equation $\sigma_{l,f} = l_f\sigma_{K,f}/K_f$.

The standard deviation, σ_x, of each experimentally determined value of x was calculated by the equation

$$\sigma_x^2 = x_1^2[\sigma_{\Delta t,1}^2(\Delta t_2)^2 + \sigma_{\Delta t,2}^2(\Delta t_1)^2]/(\Delta t_2 - \Delta t_1)^4$$

where $\sigma_{\Delta t,1}$ and $\sigma_{\Delta t,2}$ are the standard deviations of the mean values of Δt_1 and Δt_2 respectively. The experimentally determined values of x were then treated as if they were independent determinations and were combined into grand means by weighting each value by the appropriate σ_x^{-2} term. The purities in moles % (100 − x) so obtained are listed in Table 2.

The f. p. of 100% pure material was calculated by the equation $t_{f,0} = t_f + \theta x$, the grand mean values of θ and x (Table 2) being used and t_f being the initial f. p. of the actual sample. The standard deviation, $\sigma_{t,f,0}$, of $t_{f,0}$ was calculated from the expression $\sigma_{t,f,0}^2 = \sigma_{t,f}^2 + x^2\sigma_\theta^2 + \theta^2\sigma_x^2$. The standard deviation, $\sigma_{t,f}$, arises from errors in the measurement and extrapolation to zero time of the thermocouple e.m.f., and in its conversion into degrees Celsius. On the basis of a number of measurements an overall standard deviation of 0·04° has been ascribed to t_f.

It is considered, however, that the value of $t_{f,0}$ for α-picoline may not be quite so accurate as the value of $\sigma_{t,f,0}$ suggests, because of the difficulties attendant on the existence of two crystalline forms.

The literature contains 28 values for pyridine ranging from −100° to −37·5°, 5 for α-picoline from −69·9° to −64°, 4 for β-picoline from −20·8° to −17·7°, 4 for γ-picoline from 1·6° to 4·3°, and 4 for 2 : 6-lutidine from −6·3° to −5·5°. However, except for a single value for α-picoline (−66·55° ±0·08°; Freiser and Glowacki, *J. Amer. Chem. Soc.*, 1948, **70**, 2575) all the published values are for actual samples of unestablished purity.

The latent heat of fusion of pyridine in Table 2 agrees with that (21·8 ± 0·4 cal./g.) calculated from Beckmann and Waentig's results (*Z. anorg. Chem.*, 1910, **67**, 17), and is slightly less than that (24·99 cal./g.), measured calorimetrically by Parks, Todd, and Moore (*J. Amer. Chem. Soc.*, 1936, **58**, 398). It is considerably greater than the value (9·4 cal./g.) reported by Pearce and Bakke (*Iowa Acad. Sci.*, 1946, **43**, 171), which appears to be seriously in error. The latent heat of fusion of α-picoline now reported is not very accurate because of the difficulties mentioned above, but is in reasonable agreement with a value (21 cal./g.) calculated from the results of Freiser and Glowacki (*loc. cit.*), although not with that (12·9 cal./g.) of Lemmerman, Davidson, and

VanderWerf (*J. Amer. Chem. Soc.*, 1946, **68**, 1361). The values for the latent heats of fusion of β- and of γ-picoline are also not in good agreement with the last-mentioned workers' results (20·3 cal./g. and 23·7 cal./g. respectively).

Normal boiling points, values of $(\mathrm{d}t/\mathrm{d}p)_{760\ \mathrm{mm.}}$ *and latent heats of vaporization.* The normal boiling points, values of $(\mathrm{d}t/\mathrm{d}p)_{760\ \mathrm{mm.}}$, and the heats of vaporization of samples of bases purified as here described have recently been computed from vapour pressure–temperature measurements (Herington and Martin, *Trans. Faraday Soc.*, 1953, **49**, 154), and are given in Table 3. The latent heats of vaporization are uncorrected for deviations of the vapours from the ideal gas laws and the molal volume of the liquid has been neglected in these calculations. The latent heats of vaporization at the normal boiling points were calculated by using the constants of the Antoine equation which had been fitted to the experimental vapour-pressure data over a large temperature range.

TABLE 3. *Normal boiling points,* $(\mathrm{d}t/\mathrm{d}p)_{760\ \mathrm{mm.}}$, *and latent heats of vaporization.*

Compound	B. p. at 760 mm.	$(\mathrm{d}t/\mathrm{d}p)_{760\ \mathrm{mm.}}$ (° c/mm.)	Latent heat of vaporization at 760 mm. (cal./g.)
Pyridine	115·256° ± 0·002°	0·04535	109·95 ± 0·04
α-Picoline	129·408 ± 0·004	0·04695	96·92 ± 0·04
β-Picoline	144·143 ± 0·003	0·04873	100·34 ± 0·04
γ-Picoline	145·356 ± 0·002	0·04887	100·61 ± 0·03
2 : 6-Lutidine	144·045 ± 0·003	0·04818	88·16 ± 0·03

Approximately 70 determinations of the normal b. p. of pyridine have been reported, the more recent values varying almost as much as those reported before 1900, *e.g.*, from 113° (Kennard and McCusker, *J. Amer. Chem. Soc.*, 1948, **70**, 3375) to 115·5—115·8° (Corey, *ibid.*, 1953, **75**, 1172). The new value (Table 3) agrees within 0·01° with a value (115·26°) ascribed by Timmermans ("Physico-Chemical Constants of Pure Organic Compounds," Elsevier Publishing Co., New York, 1950) to Hoffman and VanderWerf (*ibid.*, 1946, **68**, 997). They, however, give only 114·1°/730 mm. The new value differs by as much as 0·11—0·32° from other values selected by Timmermans (*op. cit.*).

The normal b. p. of α-picoline obtained agrees with that reported by Freiser and Glowacki (*loc. cit.*) within the accuracy claimed by those workers (rather better than 0·1°), but differs considerably from the other values selected by Timmermans (*op. cit.*).

The values of $(\mathrm{d}t/\mathrm{d}p)_{760\ \mathrm{mm.}}$ in Table 3 for pyridine and for α-picoline are rather greater than those quoted by Timmermans.

The latent heats of vaporization determined from the vapour pressures, by assuming the ideal gas laws, should exceed the latent heats of vaporization determined calorimetrically by an amount equal to $0{\cdot}0318657[(B - V_L)T]/(\mathrm{d}t/\mathrm{d}p)$ cal./mole, where B is the second virial coefficient of the vapour, V_L is the molal volume of the liquid at the b. p., and $(\mathrm{d}t/\mathrm{d}p)$ is expressed in degrees Celsius per mm. of mercury. Since B is negative and V_L is positive it follows that the values in column 4, Table 3, should be numerically greater than the calorimetric values. Five calorimetric measurements have been reported for pyridine, ranging from 101·39 to 107·38 cal./g. The last value, to which an uncertainty of ±0·07 is ascribed (Mathews, *J. Amer. Chem. Soc.*, 1926, **48**, 452), is however probably in error as the following argument shows. Since the virial coefficients have not been measured, corrections of the calculated latent heats of vaporization for gas imperfections can be only approximate. If for pyridine the value 0·8826 for d_4^{115} (Schiff, *Ber.*, 1886, **19**, 560) is taken, the value for V_L is 0·090 l./mole, and if the second virial coefficient of pyridine at its b. p. is assumed to equal that of benzene at its b. p. (*i.e.*, 970 cm.^{3}/mole; see Francis, McGlashan, Hamann, and McManamey, *J. Chem. Phys.*, 1952, **20**, 1341), then the calorimetric latent heat should be 109·95 − 3·66, *i.e.*, 106·3 cal./mole. Since the second virial coefficient of pyridine is probably at least 970 cm.^{3}/mole, it appears likely that the value 107·38 ± 0·07 cal./g. given by Mathews is too high. Since this sample was reported to have a b. p. of 114·13°, it was probably wet, and this would result in a high latent heat.

Calorimetric measurements of the latent heat of vaporization, in cal./g., for α-picoline (90·75, Kahlenberg, *J. Phys. Chem.*, 1901, **5**, 284; 92·7/127·73°, Constam and White, *Amer. Chem. J.*, 1903, **29**, 1) and for β-picoline (94·82/141·7°, *idem, ibid.*) have been reported and, as expected, the values are smaller than those in Table 3. Work on the determination of the virial coefficients of these bases is in progress.

Densities. Measurements of densities at 20° and at 30° were made by means of a Sprengel–Ostwald pycnometer (see Bauer, "Technique of Organic Chemistry," edited by Weissberger, Interscience Publ., Inc., New York, 1949, Vol. I, p. 266). The capacity of the pycnometer was 13·5 ml. and the bores of the two limbs were 0·5 mm. and 0·2 mm. Both limbs could be closed by ground glass caps. The pycnometer design was modified slightly in that a millimetre scale was engraved on the wide-bore limb, and above this a small bulb was incorporated to allow for expansion of the liquid during weighing.

Before introduction of a sample, the pycnometer was dried by passage of air which had been dried over anhydrous magnesium perchlorate and filtered through glass wool. Each sample of base was dried by a distillation technique (Coulson, Hales, and Herington, *J.*, 1951, 2125), and it was shown that its water content after this treatment was sufficiently low to affect its density by less than 0·00001 g./ml. The sample was forced into the pycnometer, by means of a pressure of dried air, from a small vessel which was connected to the pycnometer by a ground glass joint, which was not greased. A guard-tube $[Mg(ClO_4)_2]$ was attached to both limbs of the pycnometer by means of a T-tube, and the pycnometer was placed in a thermostat water-bath. The precautions described for the exclusion of water were shown to be adequate by analysis after the experiments.

The temperature of the bath was controlled to 0·005° and standardized by means of a platinum resistance thermometer. The level of the liquid in the wide-bore limb of the pycnometer was adjusted to fall within the scale. It was necessary to place a small electric heater around the expansion bulb while the pycnometer was in the bath, to prevent condensation of sample within this bulb. Error due to evaporation of sample from the capped pycnometer while the vessel was in the balance case was avoided as follows. The position of the meniscus in the wide limb was observed at known time intervals over short periods before the removal of the pycnometer from the bath for weighing, and after return of the pycnometer to the bath. The position of the meniscus was plotted against time, and from this graph the volume the sample would occupy if it were at the bath temperature at the time of weighing was found. The usual precautions were taken in preparing the vessels for weighing, and all weights were corrected to a vacuum.

The pycnometer was calibrated at 20° and at 30° by the use of pure water (Barber, Handley, and Herington, *Brit. J. Appl. Physics*, 1954, **5**, 41). Tilton and Taylor's values for the density of water, 0·9982336 g./ml. at 20°, and 0·9956783 g./ml. at 30° (*J. Res. Nat. Bur. Stand.*. 1937, **18**, 205) were used. The performance of the pycnometer was checked by determinations of the densities of a sample of pure benzene (purity 99·99 ± 0·005 moles %), mean values found being 0·87907 ± 0·00005 g./ml. at 20°, and 0·86836 ± 0·00005 g./ml. at 30°, to be compared with 0·87903 g./ml. at 20° (Forziati, Glasgow, Willingham, and Rossini, *ibid.*, 1946, **36**, 129), and 0·86836 g./ml. at 30° (Scatchard, Wood, and Mochel, *J. Phys. Chem.*, 1939, **43**, 119).

TABLE 4. *Observed densities at* 20° *and* 30° *of pyridine,* α-, β-, *and* γ-*picoline, and* 2 : 6-*lutidine, and calculated densities and coefficients of cubical expansion at* 25°.

$[d_{25} = 0{\cdot}5(d_{20} + d_{30})\,;\ \alpha_{25} = 0{\cdot}2(d_{20} - d_{30})/(d_{20} + d_{30})]$

Compound	d_{20} (g./ml.)	d_{30} (g./ml.)	d_{25} (g./ml.)	α_{25}
Pyridine	0·98310 ± 0·00000	0·97301 ± 0·00000	0·97806	0·001032 ± 0·000000
α-Picoline	0·94432 ± 0·00000	0·93503 ± 0·00002	0·93968	0·000989 ± 0·000002
β-Picoline	0·95658 ± 0·00000	0·94736 ± 0·00002	0·95197	0·000969 ± 0·000002
γ-Picoline	0·95478 ± 0·00000	0·94561 ± 0·00000	0·95020	0·000965 ± 0·000000
2 : 6-Lutidine ...	0·92257 ± 0·00002	0·91355 ± 0·00002	0·91806	0·000983 ± 0·000003

The observed densities of the five bases at 20° and at 30° (d_{20} and d_{30}) are given together with the standard deviations in Table 4. The values at 25° (d_{25}) were obtained by linear interpolation, and the coefficients of expansion at 25°, $\alpha_{25} = (1/V)(dV/dt)$, where V is the specific volume, were calculated by means of the equation $\alpha_{25} = 0{\cdot}2\ (d_{20} - d_{30})/(d_{20} + d_{30})$.

Eighty-five published density values for pyridine, 25 for α-picoline, 14 for β-picoline, 8 for γ-picoline, and 12 for 2 : 6-lutidine, for the temperature range 20—30° were collated. Our values for pyridine at 20° and at 30° (Table 4) are somewhat higher than those selected by Timmermans (*op. cit.*), but our value at 25° (Table 4) is identical with his. In the case of α-picoline, our value for 30° (Table 4) is 0·00012 g./ml. higher than that selected by Timmermans (*op. cit.*), but the values for 20° are identical.

The coefficient of cubical expansion now found for pyridine (Table 4) equals that (0·001) reported by Dutoit and Duperthuis (*J. Chim. phys.*, 1908, **6**, 699) within the accuracy of their work, but is considerably smaller than that (0·00114) recorded by Wright (*J.*, 1940, 870) for the temperature range 25—78°. The data of Freiser and Glowacki (*loc. cit.*) lead to a value 0·00100 for the coefficient of cubical expansion of α-picoline for 20—30°.

Refractive indices. The critical-angle refractometer used (Bellingham and Stanley, London), embodied a 60° prism of refractive index 1·756269 (at 20°) for the D_1 line. Measurements were made at 0·6563, 0·5896, 0·5461, and 0·4861 μ. The scale of the instrument was calibrated and the refractive indices of the prism were determined by the National Physical Laboratory, Teddington, who also computed tables relating scale readings to refractive indices.

The refractive indices of these bases proved to be difficult to measure because not only are the bases hygroscopic but they are good solvents for greases. To exclude atmospheric moisture and avoid the presence of grease the apparatus shown in Fig. 1 was used in place of the corresponding parts supplied with the refractometer. The cell *A*, made of Pyrex glass, was thickened at the base and ground to fit the prism *F*. Care was taken in the thickening process to keep the glass as optically clear as possible, and an optical flat was ground on the outside at the point, *P*, of entry of light rays from the monochromatic source. The cell was attached to the prism by means of an amalgamated lead washer *G*. The side-arm *N* carried a guard-tube [$Mg(ClO_4)_2$]. Before introduction of sample at *N*, the assembled cell was flushed out with dry air [$Mg(ClO_4)_2$]. Since the correct alignment of the prism could not be checked by observing the reflection of the telescope graticule from the top face of the prism when the cell was attached, a small auxiliary plane mirror fastened to the underside of the prism, parallel to the top face, was used to adjust the prism.

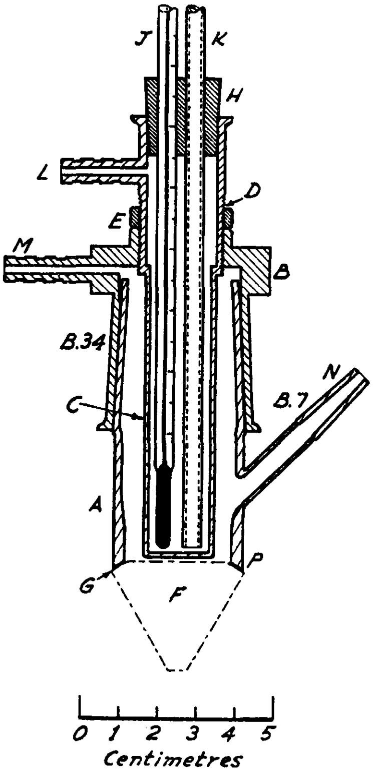

FIG. 1.

A. Pyrex glass cell.
B. Duralumin cover.
C. Duralumin well.
D. Screw thread.
E. Duralumin locking ring, with grub screw.
F. Prism.
G. Amalgamated lead washer.
H. Rubber bung.
J. Thermometer.
K. Inlet for water from thermostat.
L. Outlet for water.
M. Inlet for dry air.
N. Outlet for air, and sample inlet.
P. Window for incident light rays.

Measurements were made at 20·00° ± 0·01°, in a constant-temperature room (18—20°) with water from a thermostat circulated through the well, *C*, the prism jacket, and rubber tubing surrounding *A*. *B* and the upper part of *C* were lagged with cork. To prevent ingress of atmospheric moisture through the joints, which were not greased, a slight positive pressure of dry air was maintained within the cell.

Since it proved to be impossible to maintain and manipulate completely dry samples, measurements were made on specimens of varying water content and the results for the anhydrous compounds were obtained by graphical extrapolation. When necessary water was removed from samples by simple distillation. The water content of a sample was determined immediately after the measurement of refractive index, by infra-red spectroscopy (Coulson, Hales, and Herington, *J.*, 1951, 2125).

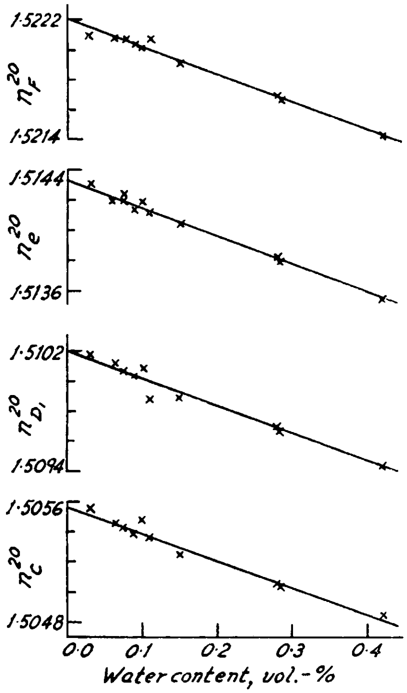

Fig. 2. *Pyridine.*

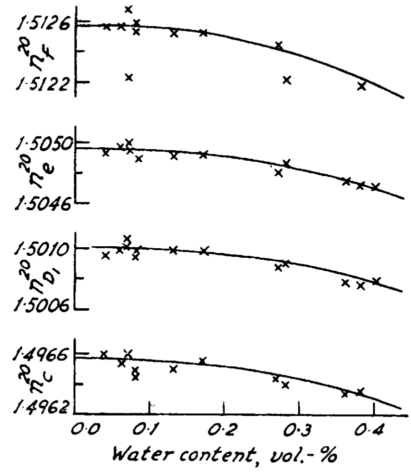

Fig. 3. α-*Picoline.*

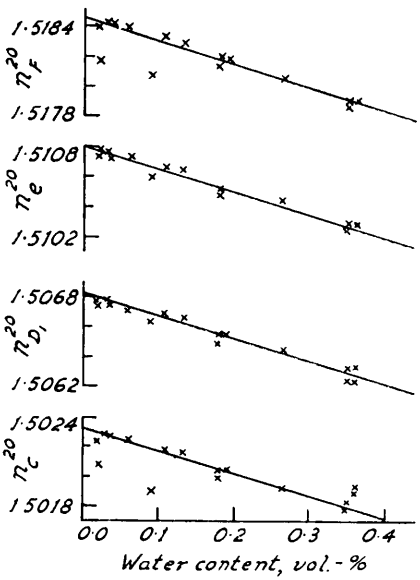

Fig. 4. β-*Picoline.*

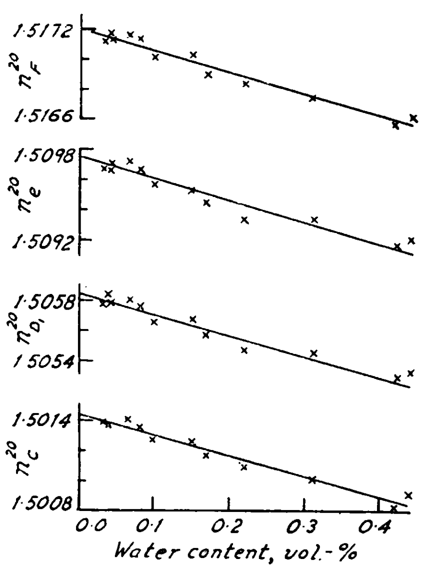

Fig. 5. γ-*Picoline.*

In Figs. 2—6 the refractive indices of the bases are plotted against water content (% by vol.). A small amount of water decreases the apparent refractive indices of pyridine and β- and γ-picoline, but is without effect on that of α-picoline. It increases that of 2 : 6-lutidine up to a concentration of at least 1% of water. Refractive index is frequently used as a criterion of purity, but the present measurements show that it gives no certain indication of the water content of α-picoline or 2 : 6-lutidine.

Extrapolation of the data in Figs. 2—6 to zero water content gave the values shown in Table 5. The standard deviation of these values is believed to be of the order of ±0·00005 unit. The molar refractivities, $[R]^{20}_{D_1}$, for the D_1 line at 20° are also shown in Table 5.

TABLE 5. *Refractive indices and molar refractivities of anhydrous bases.*

Compound	n^{20}_C	$n^{20}_{D_1}$	n^{20}_e	n^{20}_F	$[R]^{20}_{D_1}$
Pyridine	1·50556	1·51020	1·51433	1·52221	24·071
α-Picoline	1·49657	1·50101	1·50496	1·5125	29·054
β-Picoline	1·50232	1·50682	1·51080	1·51845	28·963
γ-Picoline	1·50144	1·50584	1·50975	1·51720	28·970
2 : 6-Lutidine	1·49334	1·49767	1·50153	1·50895	34·025

The usefulness of the four-constant equation $n_\lambda = n_\infty + C/(\lambda - \lambda^*)^{1\cdot6}$ for the interpolation of precise refractive-index data for hydrocarbons has been shown by Forziati (*J. Res. Nat. Bur. Stand.*, 1950, **44**, 373), and the present experimental values for the *C*, D_1, and *e* lines (Table 5) have been fitted to an equation of this type. The data for these three lines were chosen rather than any involving the *F* line, because the experimental error of measurement was believed to be greatest in the case of the *F* line. The technique of curve-fitting described by Forziati (*loc. cit.*) was employed, after the construction of suitable tables for the wave-lengths involved. The constants n_∞, *C*, and λ^* so obtained are listed in Table 6. By using these constants the refractive indices for the *F* line were calculated, and the differences between these and the observed values are shown in Table 6.

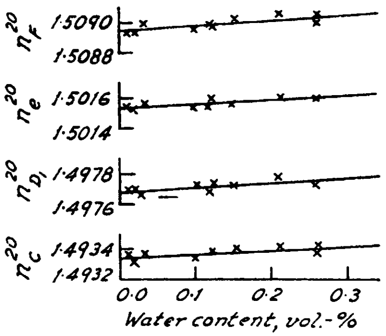

FIG. 6. 2 : 6-*Lutidine.*

TABLE 6. *Values of the constants of Tilton and Gurewitz's modification of Hartmann's equation* † *for five pyridine bases.*

Compound	n_∞	*C*	λ^*	$(n^{20}_F)_{calc.} - (n^{20}_F)_{obs.}$
Pyridine	1·48675	0·006567	0·13824	+0·00011
α-Picoline	1·47854	0·006309	0·13750	+0·0001
β-Picoline	1·48367	0·006704	0·12864	−0·00002
γ-Picoline	1·48350	0·006309	0·13582	+0·00009
2 : 6-Lutidine	1·47588	0·006054	0·14050	+0·00006

† Tilton and Gurewitz, quoted by Forziati, *J. Res. Nat. Bur. Stand.*, 1950, **44**, 373.

Twelve refractive-index values for pyridine at 20°, 7 for α-picoline, 4 for β-picoline, 5 for γ-picoline, and 3 for 2 : 6-lutidine were collated. Our value for pyridine for the D_1 line agrees with that of Rozhdestvenskiĭ *et al.* [*Trans. Inst. Pure Chem. Reagents, U.S.S.R.*, 1935, **14**, 58] for the D_1–D_2 doublet (" *D* line ") but is significantly higher than the only other value, also referring to the D_1–D_2 doublet, listed in Timmermans's book (*op. cit.*). Theoretically, for these bases, the refractive indices for the D_1 line are 0·00002 unit lower than those for the D_1–D_2 doublet. In the case of α-picoline the new value for the D_1 line is only 0·00004 unit lower than that found by Freiser and Glowacki for the D_1–D_2 doublet (*loc. cit.*), and the new value for the *e* line is only 0·00003 unit higher than that found by these workers (*loc. cit.*). If, however, the refractive index of α-picoline for the wave-length 0·4358 μ is calculated by means of the constants n_{∞}, C, and λ^* derived from the present measurements (see Table 6), the value 1·52224 is obtained. This is 0·00054 unit greater than that recorded by Freiser and Glowacki (*loc. cit.*). Thus it is very probable that their value for this wave-length is too low.

Infra-red absorption spectra. Coblentz ("Investigations of Infra-red Spectra," Carnegie Institute of Washington, 1905) described the spectra of liquid pyridine and α-picoline in the range 1—15 μ. Since then, spectra of other pyridine bases have been published, but with one exception the measurements were made on specimens of doubtful origin and purity. The exception is Freiser and Glowacki's work on α-picoline (*J. Amer. Chem. Soc.*, 1948, **70**, 2575; see also *Amer. Petroleum Inst.*, Research Project 44, spectrum Serial No. 743).

TABLE 7. *List of frequencies (cm.$^{-1}$) and rough estimates of intensities of the main absorption peaks for liquid samples.*

Pyridine		α-Picoline		β-Picoline		γ-Picoline		2 : 6-Lutidine	
702 vs	1690 w	729 s	1590 vs	708 vs	1659 w	728 s	1755 w	716 m	1471 vs
749 vs	~1745 w	751 vs	1776 w	788 vs	~1720 w	799 vs	1854 w	729 m	1584 vs
810 w	1827 w	798 m	1876 w	923 w	1838 w	872 w	1935 w	775 vs	1775 w
885 w	1876 w	883 w	1914 w	987 m	~1910 w	972 m	2025 w	889 w	~1873 w
~944 w	1926 m	972 m	1952 w	1028 s	1969 w	994 s	2200 w	972 m	1966 w
991 s	1992 w	994 s	2200 w	1106 s	2250 w	1042 s	2220 w	997 s	2230 w
1031 s	2210 w	1047 s	2380 w	1125 s	2375 w	1070 m	2310 w	1030 s	2340 w
1069 s	2300 w	1099 m	2450 w	1188 s	2465 w	1223 s	2440 w	1096 s	2450 w
1146 s	2440 w	1143 s	2600 w	1227 m	2600 w	1383 s	2740 w	1157 s	2635 w
1218 s	2590 w	1233 m	2720 w	1340 w	2755 w	1417 vs	2970 s	1224 s	2735 w
1293 w	2830 w	1291 s	2950 vs	1385 s	2895 s	~1445 s	3010 s	1248 s	2930 vs
1378 w	3030 s	1376 s	3030 vs	1414 vs	2980 s	1498 s	4120 w	1266 s	3060 vs
1439 vs	3080 s	~1440 vs	4080 w	1452 s	4065 w	1566 s	4260 w	1280 m	4060 w
1485 s	3650 w	1475 vs	4300 w	1479 vs	4315 w	1604 vs	4580 w	1374 s	4330 w
1584 vs	4070 w			1578 s	4590 w	1669 w		1456 vs	
1636 m	4600 w								

Spectrograms of our highly purified base samples were obtained with the double-beam infra-red spectrometer (Hilger D.209) described by Hales (*J. Sci. Instr.*, 1949, **26**, 359). These are very convenient for establishing rapidly the purity of samples consisting essentially of one base, while the use of certain of the absorption bands for the analysis of base mixtures has already been described (Coulson and Hales, *Analyst*, 1953, **78**, 114). Copies of the spectra of liquid and gaseous samples may be obtained on application to the Director, Chemical Research Laboratory. Lists of frequencies and rough estimates of intensities of the stronger absorption bands of liquid specimens are presented in Table 7 (s = strong, m = medium, w = weak, v = very).

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