7. *Preparation and Properties of Ethyldideuteramine and Dimethyldeuteramine.*

By E. R. ROBERTS, H. J. EMELÉUS, and H. V. A. BRISCOE.

Pure ethyldideuteramine and dimethyldeuteramine have been prepared by treating the hydrochlorides of the corresponding amines repeatedly with successive quantities of deuterium oxide, liberating the bases with lime, and fractionally distilling the products in a vacuum. Their melting points, vapour-pressure curves, and ultra-violet absorption spectra were investigated, and their vapour densities were shown to correspond to the formulæ $C_2H_5{\cdot}ND_2$ and $(CH_3)_2ND$.

For the determination of vapour densities, a novel comparative method was used in which the amine and the deuteramine, confined by mercury in glass reservoirs, were brought exactly to the same density by means of the balance, and the difference in pressure between them was observed by means of a new type of differential gauge system such that the accuracy of the determination is limited only by the precision of reading an oil-filled manometer. All necessity for thermostatic control was eliminated by enclosing both gas reservoirs in the same massive copper block and so ensuring that the temperature, although it might vary, was precisely the same in both.

Further experiments are described in which (1) ethylamine hydrochloride was treated with a large excess of deuterium oxide; (2) trimethylamine hydrochloride was treated with deuterium oxide; (3) methylamine or methyldideuteramine, mixed with deuterium, was circulated over a reduced nickel catalyst at various temperatures from 20° to 195°. These gave no evidence of replacement of hydrogen by deuterium in the alkyl group, even on a catalyst under conditions where interchange between methane and deuterium might be expected to occur freely.

Hydrogen–Deuterium Interchange in Aliphatic Amines.

When amine hydrochlorides are dissolved in water containing deuterium oxide, an exchange reaction occurs. Goldfinger and Lazareff (*Compt. rend.*, 1935, **200**, 1671), using 5% D_2O and simple aliphatic amine hydrochlorides, reported that this interchange was confined to the amino-hydrogen atoms, but their results do not exclude the possibility of a tautomerism, $CH_3{\cdot}NH_2 \rightleftharpoons CH_2{:}NH_3$, involving a molecule of the type suggested by Thomsen ("Thermochemistry," 1909) and later discussed by Henri and Lazareff in connexion with the ultra-violet absorption spectrum of methylamine (*Compt. rend.*, 1935, **200**, 829).

Since apparent equilibrium between methylamine hydrochloride and deuterium oxide, with an even distribution of deuterium among the ionisable hydrogens, was known to be reached rapidly, this method was used in preparing methyldideuteramine for an investigation of its physical properties (Emeléus and Briscoe, J., 1937, 127) but no direct proof of the constitution of the product was then obtained.

In the present work the same method has been employed to prepare ethyldideuteramine and dimethyldeuteramine as well as methyldideuteramine, and their vapour-pressure curves, melting points, and ultra-violet absorption spectra have been investigated. Their molecular formulæ have also been determined by directly comparing the vapour density of each deuteramine with that of the corresponding amine. This comparison was effected by means of a silica buoyancy balance.

The method of density measurement used in the present work differs fundamentally from the methods previously employed for similar purposes, because it achieves a very precise *comparison* of the densities of two similar gases (the ordinary and the deuterated amine) without the necessity of making a correspondingly precise determination of the absolute densities.

The silica micro-balance is used to secure equal mass concentration in the two volumes of gas, each being confined in glass by mercury and held exactly at constant volume, and both being kept at the same temperature. Under these conditions, $M_D = M_A(P_D + p)/P_D$, where M_A and M_D are the molecular weights of the amine and the deuterated amine respectively, P_D is the pressure of the deuteramine, and p the difference in pressure between the two amines.

Since M_A is taken as the standard and p is small in relation to P_D, the error of the calculated value of M_D is dependent chiefly on the error of p and only to a small extent on that of P_D. Therefore it is advantageous to measure p with much greater precision than P_D, and this is done in the present case, by using an oil gauge to measure p to $\pm0{\cdot}005$ mm. of mercury, while P_D is measured with a mercury manometer to $\pm0{\cdot}05$ mm.

As the gases compared differ but little in density and are similar in condensability and other properties, small changes of temperature will have the same effect on both, especially with respect to change of pressure and variation of adsorption on a given surface. Therefore, provided both gases are kept at the *same* temperature, any change in the pressure in the balance chamber is very exactly compensated by an equal change in the pressure of the reference gas. It is one great advantage of the new method that it thus eliminates a major source of error inherent in the ordinary method of measuring both pressures directly. This is shown very clearly by the fact that the density comparisons here recorded, although probably as precise as any previously made, did not require the use of a thermostat of any kind.

A second advantage of the new method is that it requires only simple gauges, read by inexpensive scales; whereas the attainment of a corresponding precision of reading with mercury manometers according to the usual practice requires the use of elaborate and expensive apparatus.

Though the absolute temperature of the manometer system has little effect on the comparison, it is obviously important that it shall not change appreciably during a determination. The whole system was therefore immersed in a large tank of water.

The buoyancy balance has also been used to examine the possibility of an interchange involving the alkyl hydrogen atoms. Three samples of ethylamine hydrochloride were treated with deuterium oxide (99·6%) under different conditions. The first was treated with three successive quantities of heavy water, enough being used in all to ensure almost complete substitution of deuterium for hydrogen in the amino-group, on the assumption that no rapid exchange occurred in the alkyl group; the second was treated successively with three larger quantities of heavy water according to the method used for preparing methyldideuteramine, there being enough deuterium to replace at least one of the alkyl hydrogens. In both these cases the treatment with each quantity of water was continued for about ½ hour at 30—40°. The third sample was treated with a very large excess of deuterium oxide under much more drastic conditions, being kept at 80° for 70 hours. The three specimens of deuterated ethylamine obtained from the products were found to be sensibly identical, and to have vapour densities corresponding to $C_2H_5{\cdot}ND_2$. These observations were substantiated by comparing two samples of trimethylamine, one prepared from pure trimethylamine hydrochloride and the other from a similar sample of the salt that had been treated with several quantities of deuterium oxide. The two trimethylamines were identical in every respect. Moreover, the product obtained by similarly treating dimethylamine hydrochloride with deuterium oxide had the vapour density required for $(CH_3)_2ND$.

These results afford strong evidence that in concentrated solutions of aliphatic amine hydrochlorides it is the amino-hydrogens only which take part in the exchange reaction. Under these conditions there is no indication of the tautomerism which has been suggested.

A solution of amine hydrochloride, however, is slightly acid, and it might be argued that the rate of hydrogen–deuterium interchange in the alkyl group, which would depend upon the rate of proton transfer in the tautomeric change, would be very much reduced by this acidity, though it would seem that, even so, it should become evident after sufficiently long treatment with deuterium oxide.

In order to confirm the above conclusions, it was thought desirable to investigate the interchange between deuterium and methylamine at the surface of a catalyst. Taylor and others have shown that ammonia and deuterium react readily at room temperature in the presence of synthetic-ammonia catalysts, and that deuterium and methane react at the surface of reduced nickel at 184°, whereas methane and deuteromethane react upon the same catalyst at even lower temperatures (Taylor and Jungers, *J. Amer. Chem. Soc.*, 1935, **57**, 660; Morikawa, Benedict, and Taylor, *ibid.*, 1936, **58**, 1445).

Methylamine and deuterium were therefore circulated over a heated nickel catalyst, any change in the molecular weight of the methylamine being measured by means of gas-density determination. There was no interchange except in the amino-group. This was confirmed by circulating methyldideuteramine with deuterium over the same catalyst, after which the only observable change was an increase in the purity of the deuteramine from 99·5% to 99·9% of $CH_3{\cdot}ND_2$ after two treatments.

Further experiments were made in which trimethylamine and deuterium were circulated at 170° for 3 days over a nickel catalyst; no interchange whatever occurred.

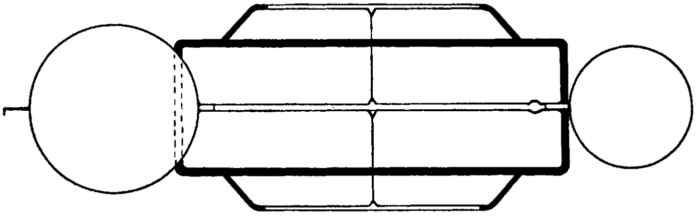
Considering Taylor's results for methane, it must be inferred that in all these cases the attachment of the adsorbed molecules to the nickel surface is effected through the amino-group. Moreover, if any tautomeric change were possible (and there is in this case no acidity to hinder it) interchange with the alkyl group should occur. The fact that none was observable is, therefore, strong evidence against the possibility of such tautomerism.

EXPERIMENTAL.

The Balance.—The balance used for determining the vapour densities of the deuteramines was of the same general design as that used by Whytlaw-Gray and Woodhead (J., 1933, 846) for the density of carbon monoxide (see also Steele and Grant, *Proc. Roy. Soc.*, 1909, **82**, 580; Gray and Ramsay, *ibid.*, **84**, 536; Aston, *ibid.*, 1914, **89**, 440; Stock and Ritter, *Z. physikal. Chem.*, 1926, **119**, 333; **124**, 204; Whytlaw-Gray, *Proc. Roy. Soc.*, 1933, **134**, 7), but differed from previous models in that while the beam, the suspension fibres, and parts of the frame were of fused quartz, as is usual, the bulbs and the major part of the frame were of Pyrex glass. It proved simple in practice to make such a composite structure by fusing the glass and quartz together in a small oxy-hydrogen flame, and the use of glass, especially for the bulbs, greatly facilitated the construction of the balance.

The beam (Fig. 1) was a fused quartz rod 50 mm. long and of 1 mm. diameter, carrying Pyrex bulbs of 19·4 mm. and 13·7 mm. diameter; their outer surfaces are in the ratio of $\sqrt{2} : 1$, and since the smaller bulb is pierced, both have the same exposed surface. The distribution of mass and surface was so arranged that a crossbar of very light quartz rod sealed on at the centre of surface was also at the centre of gravity. After exact coincidence had been obtained by careful adjustment of the beam with the aid of temporary stands, the suspension fibres were drawn, and sealed to the frame.

FIG. 1.



Final adjustments were made so that the instrument balanced in air at a little below atmospheric pressure and had a period of oscillation of 10 seconds. In contrast to the general practice, the pointer was attached to the buoyancy bulb. This enabled the compensating bulb to be pierced along the axis of the beam, thus reducing very considerably the difficulty of balancing. The set-up of the whole apparatus necessitated an end-on position for the microscope, and the pointer was accordingly bent at right angles to the axis of the beam. The balance was housed in a cylindrical glass casing 130 mm. long and of 25 mm. internal diameter, with a plane glass window cemented on at one end, and the casing was connected with the rest of the apparatus by capillary glass leads.

As will be seen from Fig. 2, the balance case B was enclosed in a heavy copper casting A, which also contained, in a separate compartment, the reservoir C for the reference gas. To protect the balance as far as possible from vibration or shock, the copper casting was supported by a three-legged stool, resting on thick piles of filter paper on a stone slab carried by steel cantilevers built in to a 24″ outer wall of the building. This arrangement proved very satisfactory, as the zero remained very nearly constant over a long period of time; and when any change not due to temperature was observed, it could always be traced to vibration of the wall caused by workmen hammering, or other exceptional violence.

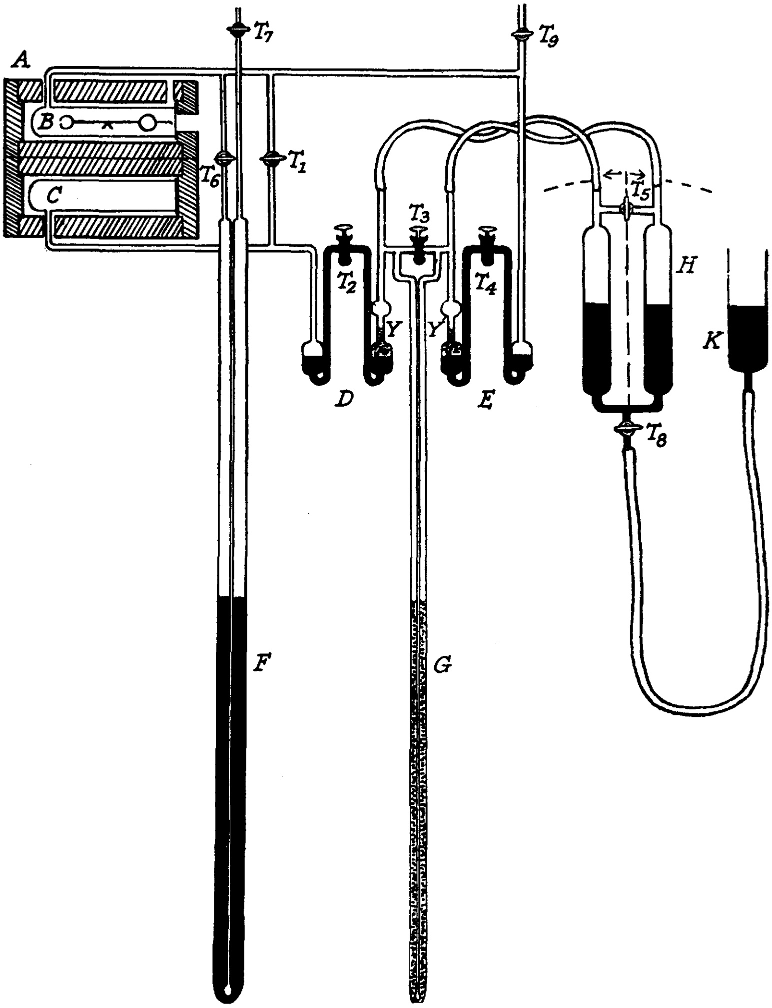
Manometer and Tank.—The general arrangement of the apparatus is shown diagrammatically in Fig. 2. The manometer system comprised a simple mercury U-tube F of 10 mm. tubing (connected by stopcocks T_6 and T_7 to the balance case and vacuum line respectively) and an oil gauge G connected to the balance case and the reference reservoir respectively through constant-volume indicators or capastats D and E having stopcocks T_2 and T_4. The capastats were essentially mercury-filled U-tubes, the centres being upswept to bring the stopcocks just into the surface of the water in the tank, and the mercury surfaces lay in bulbs of 2·5 cm. diameter. On the oil-gauge side of each capastat, oil filled the space above the mercury, and rose into a narrow tube 5 mm. in diameter (Y, Y'). Thus by applying a suitable pressure on the oil-gauge side of the indicator, the volume of the gas in the corresponding chamber, B or C, could be held at a constant value with great accuracy. A change in volume of 0·02 c.c. could be detected easily, and as the volume of the chamber was about 130 c.c., the maximum change of pressure due to undetected variations in volume could not exceed about 0·005 mm. Hg.

The two sides of the oil gauge, which could be bridged through stopcock T_3, were connected by $\frac{3}{8}''$ india-rubber pressure tubing to an oil-gauge pressure adjuster H, consisting of a mercury U-tube connected to the reservoir K by stopcock T_8 and bridged through the stopcock T_5, whereby the two sides could be isolated at will. By adjusting the amount of mercury in the U-tube H and by tilting it also, any desired combination of pressures on the two sides of the oil gauge could be obtained. The whole assembly H was therefore carried on a mounting which could be tilted by means of a circular rack and pinion, and as this was geared very low, a very delicate adjustment of the oil levels was possible.

The balance case and reference reservoir were connected to each other and to the main vacuum line by stopcocks T_1 and T_9 respectively.

The manometer system, which, for compactness, was bent four times at right angles, so as to be in three parallel parts, thus |‾‾|__|, was all enclosed in a tank of 1″ teak, having $\frac{1}{4}''$ plate glass back and front, clamped on by $\frac{3}{8}''$ bolts and $\frac{1}{2}''$ teak strips 3″ wide. These were kept from buckling by 1″ × 1″ teak struts alongside each bolt, and the tank was rendered watertight by a gasket of ⅜″ india-rubber pressure tubing between the glass and the wood. The inside of the tank, which measured 150 × 250 × 1000 mm., was given three coats of waterproof varnish. The tank held about 38 l. of water and no variation could be detected in its temperature during the 2—3 hours required for a determination. It was not necessary to stir the water.

FIG. 2.



Method of Operation.—The zero levels of the oil in the capastats are first determined by opening each to the atmosphere on both sides. Then, with T_2 and T_4 shut, the balance case *B*, the reference chamber *C*, and the mercury gauge *F* are completely evacuated through T_7 and T_9. With T_7 shut, the reference gas is then allowed to enter *B* and *C*, its pressure is adjusted until the balance pointer is at zero, and T_9 is then shut. To facilitate this adjustment, the gas is taken from a reservoir of cooled liquid through two stopcocks in series with a small reservoir between them. By adjusting the temperature of the cooled liquid, its vapour pressure is made slightly less or more than the pressure in the chambers so that, by manipulation of the stopcocks, gas may be passed from or to the chambers in small amounts with great precision. Thus a volume adjuster of the usual type is not required.

The total pressure in *H* is now made approximately equal to that in the balance case, and T_2 and T_4 are cautiously opened. The pressure in *H* is then adjusted to bring both capastats to zero again. As T_3 and T_5 are still open, the oil gauge will read zero, and the pressures and levels in both sides of *H* will be equal. T_1, T_2, T_4 are now closed, thus isolating a quantity of reference gas at its balancing pressure in the chamber *C*.

The balance case is next evacuated for 1—1½ hours to remove all traces of the reference gas, and then rinsed with a small quantity of the gas under investigation, and again evacuated for 10 minutes. Then the gas is admitted, and its pressure adjusted until the balance is again at zero. Stopcocks T_3 and T_5 are now shut, and by tilting *H* a difference of pressure such as would be anticipated from the difference in densities of the gases is set up between the two sides of the oil gauge. T_2 and T_4 are now cautiously opened, and the total and relative pressures above the oil gauge are adjusted until the oil levels in the capastats are again at zero. The difference in the oil levels in the gauge, which is the difference between the balancing pressures of the two gases, is read on a silvered-glass scale to 0·005 mm. Hg. At the same time the absolute pressure of the gas is read on the mercury manometer to 0·05 mm. by means of the same glass scale.

The manometric system was calibrated by comparing the balancing pressures of pure ethylene and dry air freed from carbon dioxide. The ethylene had been purified by low-temperature fractionation, and the air was admitted through a tube containing 10″ of potash pellets and 6″ of phosphoric oxide, followed by a trap cooled to − 78°.

Several determinations were made, the pressure differences read on the oil gauge all lying within a range of 0·2 mm. of oil. The mean value obtained for the difference in balancing pressures of the two gases was 29·66 cm. of oil when the balancing pressure of air was 65·27 cm. of mercury. Since the densities of air and ethylene are 14·475 and 14·026 respectively, the calculated balancing pressure of ethylene is 67·365 cm. of mercury. Thus 29·66 cm. of oil are equivalent to 2·095 cm. of mercury.

To check the balance for compensation of surfaces, ethylamine was balanced against dimethylamine a number of times. No difference in balancing pressure between the two was ever observed. Having regard to the fact that the b. p.'s of these substances are 16·5° and 6·9° respectively, and that the comparison was made at 18°, it is evident that any difference in adsorption on the two sides of the balance is too small to have an appreciable effect on the density comparisons.

In some cases, where there was insufficient deuteramine to fill the balance case and the mercury manometer, the balancing pressure of the amine was read instead of that of the deuteramine. In such cases care was taken that the temperature did not change appreciably during the determination.

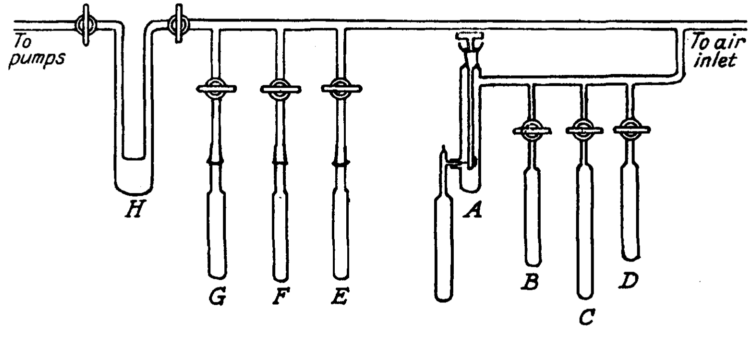
The following examples give an indication of the nature of the readings in an actual experiment :

Sample.	Balancing pressure, cm. of Hg.	Difference in balancing pressures, cm. of oil.	Mol. wt.
$CH_3{\cdot}NH_2$	58·390	49·40	31·048
$CH_3{\cdot}ND_2$	54·900	—	33·021
$(CH_3)_2NH$	40·220	12·24	45·075
$(CH_3)_2ND$	39·356	—	46·065

Interchange in Solution.

Preparation of Deuteramines.—General. The preparations were carried out in a vacuum apparatus (Fig. 3). It was possible to use ground joints and glass stopcocks, because experience showed that if these were carefully lubricated with Apiezon *M* grease, excess of lubricant being avoided, no difficulty was experienced through absorption of the amines.

FIG. 3.



Deuterium oxide was distilled through the capillary opener *A* into the storage vessel *B*; the amine hydrochloride was weighed into *E*, and treated with successive quantities of heavy water, whose volumes were first measured by distilling them into the graduated tube *C*.

After air, purified by passing over solid potassium hydroxide and phosphoric oxide, had been admitted, the vessel *E* was detached, an excess of freshly ignited quicklime was added, and *E* was quickly replaced and evacuated, the trap *H* being cooled to condense any amine. The amine was expelled by heating to 150—200°, collected in *H*, and subsequently condensed into *F*, which contained a further quantity of quicklime, and so left overnight. This treatment was found to be inefficient, since quicklime has apparently little power to retain water in a high vacuum. In subsequent preparations, drying was effected by metallic sodium.

The amines were purified by fractional condensation in a Stock fractionating apparatus (*Ber.*, 1917, **50**, 989), stopcocks being used instead of mercury valves. Purification was considered to be complete when the middle fraction showed no change in its vapour-pressure curve on further fractionation.

Ethyldideuteramine. Sample I. Ethylamine hydrochloride (B.D.H.) was recrystallised three times from rectified spirits and finally from absolute alcohol. It was dried on filter-papers, desiccated over calcium chloride, and stored over this reagent after the large crystals had been crushed.

0·760 G. was weighed into *E*. This weight was obtained by weighing *E* empty, then charging it with salt and evacuating it to constant weight, a procedure necessitated by the deliquescent nature of the hydrochloride. This was treated successively with 0·58, 0·79, 0·64, 0·59, 0·62, and 0·63 c.c. of water containing 99·6% D_2O. Each lot of water was allowed to melt, dissolving the salt, and then kept at 30—35° for 30 minutes, after which it was pumped off into *H* and distilled back into the storage vessel *D*. Each quantity of water is approximately 3 mols. per mol. of amine hydrochloride. If, as is supposed, the interchange is limited to the three amino-hydrogen atoms, then at equilibrium in the first treatment the deuterium : hydrogen ratio will be 2 : 1, after a second treatment it will be 2·67: 0·33, and after the sixth treatment it will be 2·996 : 0·004.

The amine, liberated and partially dried by quicklime, was distilled at — 78° through a condenser held at — 110° and to a second condenser held at — 194°. Only a trace of more volatile impurity was found, but owing to the incomplete removal of water by the lime, there was a considerable tail fraction, the purification of which was very tedious. After four redistillations of the main fraction, the vapour-pressure curve became constant. The amine was stored in a glass globe attached to the apparatus by a stopcock.

Sample II. 1·294 G. of the same pure hydrochloride were weighed into *E* and treated with 0·95, 0·96, and 0·95 c.c. of the 99·6% D_2O, each solution being held at 40° for 30 minutes. Calculation shows that if the interchange is confined to the amino-group, the deuterium : hydrogen ratio in the product should be about 98 : 2. The final solution was divided into two portions, and the water pumped off from both. One portion of the salt was used to prepare the amine as described for Sample I and gave sensibly the same vapour pressure curve.

Sample III. To the second portion of heavy salt a large excess of 99·6% D_2O, approximately 50 mols., was added, and the solution was kept at 80° for 10 periods of 7 hours each, with the intervening overnight periods at room temperature. This experiment was carried out in the vessel *G*, which was fitted with a refluxing device. If the alkyl hydrogen atoms were taking part in a slow interchange reaction, this treatment should have sufficed to detect it. The amine was generated, purified, and stored as before; its vapour-pressure curve was identical with that of Sample I.

Ethylamine. For purposes of comparison pure ethylamine was prepared in the same way. The vapour-pressure curve of the purified product was identical with that described by Pohland and Mehl (*Z. physikal. Chem.*, 1933, **164**, 48).

Dimethyldeuteramine. Dimethylamine hydrochloride (B.D.H.) was recrystallised from rectified spirits four times, the final product being pure white. It was dried and stored over calcium chloride. 1·4 G. were weighed into *E*, and treated with 0·61, 0·58, 0·60, 0·59, and 0·66 c.c. of 99·6% D_2O, these quantities each nearly corresponding to 2 mols. of water to one of hydrochloride. The calculated replacement of hydrogen by deuterium is 99·5%. The amine was liberated and partly dried by quicklime, and then further dried at 0° by metallic sodium introduced into the apparatus in a thin sealed phial which was broken in a vacuum. It was finally purified by distillation from — 78° through a condenser at — 115° into a second condenser at — 194°. Three fractionations sufficed to give a product having a constant vapour-pressure curve.

Dimethylamine. A sample of pure dimethylamine was prepared in the same way. The difficulty of removing traces of trimethylamine (which still appear to be present even after very careful fractionation, as shown by absorption-spectrum observations, Jolley, Ph.D. Thesis, London University) was overcome by holding the mixture at — 90° to — 95° in a vacuum for some time. At this temperature trimethylamine (which freezes at — 117·2°) still has an appreciable vapour pressure and can be distilled off, while dimethylamine, which freezes at — 93°, is not appreciably volatile. The dimethylamine obtained had a vapour-pressure curve identical with that described by Simon and Huter (*Z. Elektrochem.*, 1935, **41**, 28).

Trimethylamine. Two samples of trimethylamine were prepared. The first was liberated from the hydrochloride by the action of quicklime at about 50—100°, dried with quicklime and then with sodium, and finally fractionated from — 78° to condensers at — 130° and — 194°. The second was prepared in the same way except that the hydrochloride had been treated with five successive quantities of 99·6% D_2O, each being approximately 3 mols. of water to one of hydrochloride. Thus there was sufficient deuterium to give a 90% interchange with the alkyl hydrogens, if this were possible.

The physical properties of these two preparations were compared carefully, and found to be identical. Moreover, the vapour-pressure curves were the same as those obtained by Simon and Huter (*loc. cit.*). The m.p., however, about which there has been some uncertainty, was found to be — 117·2° ± 0·1°.

Physical Properties of the Deuteramines.

1. *Vapour Density and Extent of Interchange.*—The vapour densities of the deuteramines prepared were compared with those of the corresponding ordinary amines by the method and technique already described. The results are summarised in Table I. They show unequivocally that the deuterium does not enter the alkyl groups, although it almost completely replaces the amino- and imino-hydrogen. The ethyldideuteramine prepared by the ordinary method is shown to contain over 99% of $C_2H_5{\cdot}ND_2$, which is near the maximum obtainable when using 99·6% D_2O. The second sample contained about 98% $C_2H_5{\cdot}ND_2$, since it was only treated three times with deuterium oxide. The third sample, obtained from hydrochloride drastically treated with a large excess of heavy water, is practically identical with sample I.

This evidence is substantiated by the measurements with dimethyldeuteramine. The density of this again shows replacement of about 99·5% of the ionisable hydrogen by deuterium. If further evidence were necessary, it is provided in a striking fashion by the two samples of trimethylamine, one treated with deuterium oxide and one untreated. There was not the slightest indication of any difference in the densities of these two gases when balanced against each other.

Methyldideuteramine prepared by the procedure described in an earlier communication was found to be practically pure $CH_3{\cdot}ND_2$, thus justifying the conclusion based on consideration of other physical properties.

TABLE I.

Sample.	Balancing press. (from Hg gauge).	Hg equiv. of oil-gauge reading.	Balancing press. (calc. from oil gauge).	*M.**
$C_2H_5{\cdot}NH_2$	392·60 ± 0·05	—	—	45·085
$C_2H_5{\cdot}ND_2$, I	—	15·959 ± 0·005	376·65	$46{\cdot}99_2$
,, II	—	15·702 ,,	376·90	$46{\cdot}96_1$
,, III	—	15·920 ,,	376·68	$46{\cdot}99_0$
$(CH_3)_2NH$	402·20 ,,	—	—	45·085
$(CH_3)_2ND$	—	8·641 ,,	393·56	46·065
$(CH_3)_3N$, I	306·85 ,,	—	—	59·103
,, II	—	0·000 ,,	306·85	$59{\cdot}10_3$
$CH_3{\cdot}NH_2$	593·95 ,,	—	—	31·048
$CH_3{\cdot}ND_2$	—	34·954 ,,	559·0	$33{\cdot}02_2$

* The molecular weights of the reference gases are calculated from the atomic weights C = 12·010, H = 1·008, and N = 14·008.

2. *Vapour Pressure and Boiling Point.*—For measuring the vapour pressure, Stock's well-known method was employed, and Emeléus and Briscoe's technique was followed (J., 1937, 127). Ten or twelve readings were obtained for each of the three ethyldideuteramine

samples, all in the region where the vapour pressure changes rapidly with temperature (— 10° to + 15°), and the curves were plotted on a single diagram : they were identical over this range. The complete vapour-pressure curve of sample I was drawn over the range — 60° to +15°, 44 measurements being made. Temperature was measured by a standardised mercury thermometer (+15° to — 10°), a sulphur dioxide vapour-pressure thermometer (— 10° to — 40°), and an ammonia vapour-pressure thermometer (— 40° to — 60°). As a further precaution against error, samples I, II, and III were mixed, and the vapour-pressure curve again determined; it was found to be identical with that of sample I.

In addition to the p–T curve the log p — $1/T$ curve was plotted, and from both these the b. p. was obtained by extrapolation. The values from the two curves are in good agreement. The results are summarised under (i) and (ii) respectively in Table II, where the m. p.'s are also recorded.

TABLE II.

	B. p.				B. p.		
Sample.	(i).	(ii).	M. p.	Sample.	(i).	(ii).	M. p.
$CH_3{\cdot}NH_2$	−6·2°	−6·1°	−93·1°	$C_2H_5{\cdot}NH_2$	16·55°	16·6°	−81·0°
$CH_3{\cdot}ND_2$	−5·2	−5·1	−89·2	$C_2H_5{\cdot}ND_2$	17·5	17·4	−78·5
$(CH_3)_2NH$	6·94	6·9	−93·0	$(CH_3)_2ND$	7·75	7·7	−91·1

TABLE III.

Ethyldideuteramine.				Dimethyldeuteramine.			
t.	p, mm.	t.	p, mm.	t.	p, mm.	t.	p, mm.
15·5°	700·7	−23·6°	96·7	5·5°	692·7	−33·2°	94·4
8·6	526·9	−41·1	32·3	0·0	547·5	−48·3	33·2
0·0	354·3	−54·4	12·2	−11·8	310·8	−62·5	10·7
−10·8	207·1	−60·0	7·7	−23·2	168·1	−68·6	5·9

Table III gives a selection of the actual vapour-pressure measurements for each deuteramine, and Table IV gives a few selected data for ethylamine and dimethylamine and the corresponding deuterated amines, to show the general trend and magnitude of the vapour-pressure differences.

TABLE IV.

t.	$C_2H_5{\cdot}NH_2$.	$C_2H_5{\cdot}ND_2$.	Diff.	$(CH_3)_2NH$.	$(CH_3)_2ND$.	Diff.
−50°	19·0	17·5	1·5	29·0	27·5	1·5
−30	72·2	69·5	2·7	117·0	113·0	4·0
−20	130·5	126·5	4·0	209·0	199·5	9·5
−10	223·0	216·5	6·5	351·2	338·8	12·4
0	369·9	354·3	15·3	562·1	547·5	14·6
5	465·8	445·5	20·3	701·8	677·5	24·3
10	582·5	557·0	25·5			

3. *Ultra-violet Absorption Spectra.*—The ultra-violet absorption spectra of ethyldideuteramine and dimethyldeuteramine were photographed, and the positions of the principal bands measured, a Hilger small quartz spectrograph (E531) being used. The amine, at various pressures, was contained in a quartz absorption cell 5 cm. long. The light source was a water-cooled Wood's hydrogen tube, operated by 0·25—0·3 amp. at 5000 volts.

Ethyldideuteramine. Thirty bands were measured, the copper arc being used as reference. The general character of the spectrum, which resembles that of ethylamine but is more crowded, appears to be very complex. The bands seem to fall into three series, in each of which $\Delta\nu$ is about 630 cm.$^{-1}$ (cf. 669 for ethylamine), but it is possible that a more satisfactory analysis would result if alternate bands in each of these series were considered separately, making six systems of relatively intense bands. For this, however, it is desirable to use an instrument of higher dispersion.

The bands, which extend from about 2400 to 2050 A., are of at least three different intensities, somewhat diffuse, and appear, at least in the most intense bands, to be degraded towards the ultra-violet. In addition to the (intense) bands measured, there are a number of relatively weak bands which could not be measured, and are not given in the table. A comparison with the absorption spectrum of ethylamine shows many bands nearly coincident, but until more is known about both spectra, the reality of this coincidence remains doubtful and its meaning obscure.

The values for λ, ν, and Δν are given in Table V.

Dimethyldeuteramine. The spectrum of this compound is extremely complex. There are apparently three main series of bands, though again it is doubtful whether these should not in fact be regarded as six series. In addition there are at least three more systems, showing very much weaker absorption, which were not measured. The measurements of the band heads of the three main systems are given in Table V.

TABLE V.

Ethyldideuteramine.

λ, A.	ν, cm.$^{-1}$.	Δν.		
2392	41,805			
2357	42,426	621		
2348	42,590			
2319	43,127	701		
2310	43,290		700	
2300	43,478			
2289	43,682	555		
2272	44,013		723	
2268	44,090			612
2257	44,305	623		
2244	44,564		551	
2236	44,724			634
2227	44,906	601		
2218	45,104		640	
2205	45,356			632
2198	45,468	562		
2186	45,742		638	
2174	45,997			641
2168	46,123	655		
2156	46,382		640	
2147	46,578			581
2139	46,758	635		
2126	47,040		658	
2120	47,170			592
2110	47,393	635		
2100	47,619		579	
2090	47,847			677
2082	48,029	636		
2071	48,285		666	
2063	48,473			626
2055	48,661	632		

Dimethyldeuteramine.

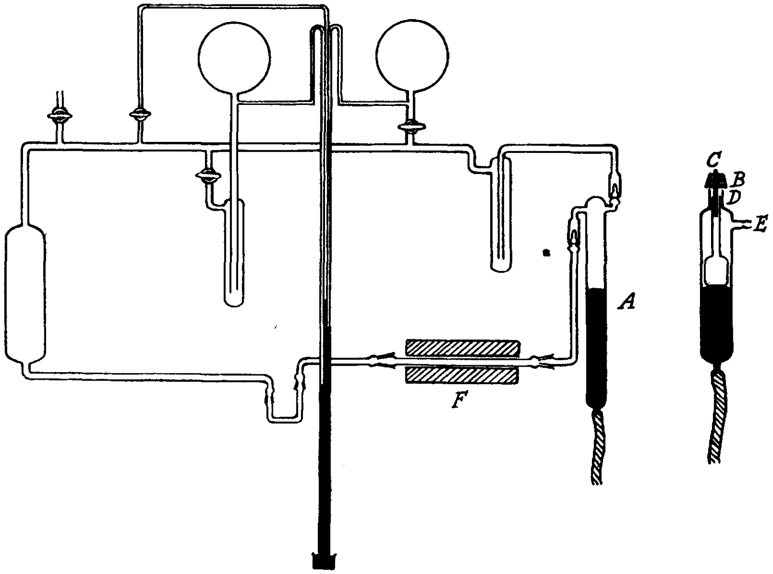
λ, A.	ν, cm.$^{-1}$.	Δν.		
2237	44,704			
2228	44,887			
2218	45,091			
2212	45,213	509		
2207	45,316		429	
2190	45,662			571
2182	45,852	639		
2178	45,912		526	
2168	46,123			461
2160	46,296	444		
2155	46,404		492	
2146	46,599			476
2137	46,849	553		
2131	46,926		522	
2121	47,158			559
2115	47,285	436		
2109	47,525		499	
2099	47,633			475
2092	47,823	538		
2086	47,934		509	
2076	48,266			633
2070	48,309	486		
2064	48,449		515	
2052	48,722			456
2049	48,806	499		
2042	48,972		523	
2029	49,291			569
2027	49,338	532		
2019	49,537		565	
2010	49,751			560
2004	49,905	567		
1998	50,014		477	
1988	50,395			644
1983	50,426	521		
1977	50,577		563	
1963	50,941	515		

Further work on these spectra is in progress.

Interchange at a Catalytic Surface.—As already mentioned, such a stable molecule as methane will interchange with deuterium at the surface of reduced nickel at 184°, whilst ammonia and deuterium react readily on synthetic-ammonia catalysts even at room temperature. It would appear, therefore, that methylamine should react with deuterium on catalytic surfaces, and accordingly a series of experiments was undertaken with the primary object of ascertaining if catalytic interchange could effect substitution of deuterium for hydrogen in the alkyl as well as in the amino-group of methylamine. The method employed was to circulate the amine mixed with deuterium over a heated nickel catalyst and measure the extent of interchange by density determinations with the buoyancy balance.

The system shown diagrammatically in Fig. 4 was designed to circulate gases over the heated catalyst at any desired pressure. The circulating pump *A* consisted of a mercury **U**-tube whose limbs were connected by 6 feet of $\frac{3}{8}$″ bore india-rubber pressure tubing. The limb which formed part of the circulating system had ground glass inlet and outlet valves. The other limb was fitted with a floating piston which opened and shut a poppet valve as the mercury rose and fell. This valve was a rubber bung *B* on a guide rod *C* which fitted loosely in the neck of the float, the bung resting on the ground end of the narrow neck *D* of the **U**-tube limb. When steady suction is applied by means of a water pump connected with the side tube *E*, the mercury rises in the outer limb until the float lifts the valve and so admits air, when the mercury falls again. This cycle repeats itself indefinitely with a concomitant oscillation of the mercury column which, therefore, acts as a piston in the pump limb. The rate of pumping can be varied over a wide range by adjusting the suction and varying the loading of the float valve, and the device proved entirely reliable when running unattended over long periods. It has the advantages over some other similar contrivances that, (*a*) owing to the size of the outer limb and the use of a flat-faced valve, there is practically no risk of sucking the mercury over into the suction pump, and (*b*) as the relative positions of the bulbs can be adjusted, the pump can circulate gas at any pressure at which the valves will operate.

FIG. 4.



Pure deuterium was prepared by electrolysis of 99·6% deuterium oxide containing dissolved sodium peroxide as electrolyte in a cell devised to minimise the bulk of electrolyte and facilitate the collection of the deuterium in an evacuated bulb. The deuterium first evolved was rejected, and the pure gas evolved later was collected and mixed with methylamine in measured proportions in the circulating system. The mixture was circulated over a hot nickel catalyst in the furnace *F*, and at the end of the experiment condensable gases were frozen out and the rest pumped out; the former were then examined.

The catalyst was prepared from pure nickel gauze which had been freed from grease by repeated treatment with ether (*d* 0·720) and then oxidised in the catalyst tube at 420° for 3 hours. The oxygen, obtained from a cylinder, was dried by passing through two bubblers of concentrated sulphuric acid. The partly oxidised nickel was then reduced at 250° for 6 hours with cylinder hydrogen which had been purified by passing first over heated palladised asbestos and then through a freezing bath of alcohol cooled with solid carbon dioxide. The oxidation and reduction process was repeated three times. When the catalyst was to be used for deuterium, the final reduction was carried out using that gas.

Preliminary experiments with methylamine, alone and with hydrogen, were carried out to find the temperature at which the interchange could be run without fear of decomposing the amine, decomposition being ascertained by means of the vapour-pressure curve. There was no decomposition below 220°; but at 230°, decomposition was evident, though not extensive, at the end of a 24-hour run.

Methylamine and deuterium were circulated in various proportions while the catalyst was held at various temperatures between 20° and 195°, the experiment usually being allowed to run overnight (16—24 hours). The amine was checked for purity by its vapour pressure. The extent of interchange was found by comparing the vapour density with that of pure methylamine, the buoyancy balance being used as already described.

For reasons of economy, a quantity of pure methylamine was circulated successively with a number of small quantities of deuterium, and the density of the amine was checked after each experiment. This produced an amine which corresponded in density approximately to $CH_3{\cdot}ND_2$, but the progressively smaller fraction of deuterium taken up suggests that, as in the case of the solution, the interchange is confined to the amino-group. The results of the progressive deuteration are shown in Table VI.

TABLE VI.

Temp.	Time, hrs.	p_D, mm.	p, amine, mm.	Value of x in $CH_3{\cdot}NH_xD_{2-x}$.
158°	16	202	388 $CH_3{\cdot}NH_2$	1·57
158	16	166	190 $CH_3{\cdot}NH_2$ +298 product *	1·53
158	16·5	145	480 ,,	1·33
158	4·5	156	466 ,,	1·32
150	16	151	468 ,,	1·18
150	4	151	437 ,,	1·14
170°	18	194	366 product	0·89
170	18	161	366 ,,	0·54
175	23	143	362 ,,	0·33
185	18	115	344 ,,	0·20
185	16·5	92	344 ,,	0·08
190	17	72	329 ,,	0·03

* The " product " is in each case that resulting from the previous run.

To confirm this conclusion, a sample of methyldideuteramine as pure as possible was prepared by the ordinary method and circulated with an approximately equal volume of deuterium over a nickel catalyst at 200° for 66 hours. The amine was balanced against the original deuteramine and found to have become a very little heavier (cf. Tables VII, IV). Calculation showed that the increase in density corresponded with an increase in purity from 99·6% to 99·9%. A further treatment produced very little change, and a third treatment had no measurable effect. A comparison of the vapour-pressure curves of the deuteramine samples, before and after this treatment, showed them to be identical. Table VII summarises the whole of the experiments with the circulator.

TABLE VII.

Summary of experiments with the circulator and nickel catalyst.

Temp.	Period, hrs.	Result.
I. Methylamine.		
20°	66	No decomp.
120	8	,,
220	24	,,
230	8	Little decomp.
II. Methylamine and hydrogen.		
160	6	No decomp.
220	16	Little decomp.
III. Methylamine and deuterium.		
20°	240	No interchange
195 *	24	,,
120	24	,,
158 to 190		(See Table VI for results.)
IV. Methyldideuteramine and deuterium.		
195	24	No alkyl exchange
195	66	,, ,,
V. Trimethylamine and deuterium.		
184	72	No interchange

* This run was conducted without a catalyst.

The inability of the alkyl group in methylamine to take part in exchange reactions with deuterium under the conditions described may be due to the pronounced electronegative character of the amino-group. This would become strongly adsorbed on the surface of the nickel, where the interchange occurs, whereas the alkyl group would have less intimate contact with the surface. This applies equally whether the amino-group be completely deuterated or not, so that methyldideuteramine would be expected to take up deuterium only very slowly, if at all, unless it were capable of existing in tautomeric forms. The results seem to show clearly that this is not the case.

The general result of these experiments opens up the exceedingly interesting problem of the effect of substituents upon the interchange of deuterium and hydrogen at catalyst surfaces, and suggests some enquiries of fundamental importance in the chemistry of both aliphatic and aromatic substances.

Grateful acknowledgment is made of a grant from Imperial Chemical Industries, Ltd., towards the cost of the apparatus used in this work.

IMPERIAL COLLEGE, LONDON, S.W. 7.

[*Received, November 5th,* 1938.]