

was only 93.2% (*Helv. Chim. Acta*, 1935, **18**, 1464; 1936, **19**, 336); this corresponds to 30% of pentadeuterobenzene and appreciable amounts of less highly deuterated derivatives (see Fig. 1). We prepared hexadeuterobenzene by the exchange reaction between benzene and sulphuric acid (*Nature*, 1934, **134**, 734) and for more than a year past have experimented with material containing only 1% of pentadeuterobenzene (*ibid.*, 1935, **135**, 1034; **136**, 301). In particular, material of at least this degree of purity has been used for the spectroscopic work described in the succeeding papers.

Hydrogen Exchange between Benzene and Sulphuric Acid.—From the theory of aromatic substitution and our empirical knowledge of the behaviour of sulphuric acid as a condensing agent, we predicted that this exchange would occur and could be made to proceed more rapidly than sulphonation. Our first experiments were with 65 mols. % aqueous sulphuric acid (*i.e.*, 35 mols. % of water); the exchange is rapid but an appreciable amount of sulphonation occurs under these conditions, and it is uneconomical to proceed to the limit of deuteration by repetition with this reagent. For preparative purposes we have used aqueous acid of 52 or 51 mols. % concentration and certainly with the latter the recovery of benzene is practically quantitative. It would appear that sulphonation ceases when the amount of water is sufficient to form $[\text{H}_3\text{O}]^+[\text{HSO}_4]^-$, where, of course, H stands for any mixture $^1\text{H}_x + ^2\text{H}_{(1-x)}$. At greater dilutions, *e.g.*, with 40 mols. % aqueous acid, no sulphonation at all occurs, but the exchange still takes place though at a rather low rate. The reactions were performed by merely shaking the reagents together at the room temperature, and with 51% acid equilibrium in exchange was reached well within the usual time allowed, *viz.*, 3–4 days. We have not made an accurate determination of the exchange equilibrium constant, $K = [\text{C}_6\text{D}_6][\text{H}_2\text{SO}_4]/[\text{C}_6\text{H}_6][\text{D}_2\text{SO}_4]$, but our observations show that it is slightly greater than unity. The successive equilibrations were followed in the first instance by combustion of the benzene samples and pyknometric determination of the density of the water thus produced. Later, when the density of pure hexadeuterobenzene was known and a density–composition curve had been plotted for the partly deuterated intermediate mixtures, the whole process could be followed more conveniently by direct determinations of the densities of the benzenes.

The reagent was prepared from pure sulphur trioxide and deuterium oxide (containing 99.95 atoms % deuterium). The former was distilled (0.05 mm.) into a tared bulb, weighed, and distilled into the appropriate quantity of deuterium oxide, all-glass apparatus being used. After titration with standard sodium hydroxide, the strength was adjusted if necessary by a further small addition either of deuterium oxide or of a previously prepared stronger acid, and again checked by titration. Pure, thiophen-free benzene was thoroughly dried with phosphoric oxide and distilled. It was added to the sulphuric acid reagent in the proportion $\frac{1}{3}\text{C}_6\text{H}_6 + 3\text{D}_2\text{O} + c\text{SO}_3$ (*c* has already been defined), shaken as described above, transferred by distillation in a vacuum to an equal amount of a fresh sample of the same reagent, and shaken again. After four repetitions, the benzene was transferred to a bulb containing barium oxide previously heated for 1 hour at red heat in a high vacuum. After contact for 12 hours with this reagent, the sample was transferred to a bulb containing phosphoric oxide, from which, 15 mins. later, it was distilled into the stock bulb. All transferences of benzene were made by distillation in an oil-pump vacuum, the gas-line being provided in advance with the necessary number of bulbs and constrictions for sealing. Liquid air was used to prevent access of oil vapours from the pump and to cool the benzene whilst sealing. This procedure gives a benzene containing not less than 99.8 atoms % deuterium, but by stopping at the intermediate stages samples could be obtained suitable for measurements designed to correlate physical properties with deuterium content. For the earlier stages of some of the later preparations we used “spent” acid derived from the later stages of the earlier preparations.

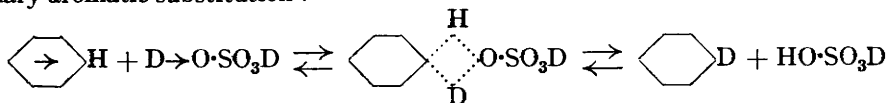
For the isotopic analyses, about 0.1 g. of the sample was accurately weighed on a micro-balance in a small glass bulb with a long capillary neck which was sealed immediately after weighing. This bulb was then broken under the surface of about 9 c.c. (accurately weighed) of pure ordinary benzene contained in a stoppered bottle. The whole of the benzene mixture was then burnt over red hot copper oxide in a stream of dry nitrogen. The combustion water, collected at -78° , was purified by a single distillation, without boiling, in an evacuated all-glass apparatus, a method by which the repeated distillations previously necessary (Day, Hughes, Ingold, and Wilson, *J.*, 1934, 498, 1593) were avoided. Details of the cleaning of apparatus and

of the pyknometry are given in the papers cited. The atomic percentage of deuterium in the original sample is

$$\frac{P(W + w) - 0.015W}{[w + 0.0001158W - 0.000772PW]}$$

where w and W are respectively the weights of the benzene sample and of the ordinary benzene used as diluent, each duly corrected for buoyancy in atmospheric air, and P is the atomic percentage of deuterium in the combustion water, corrected, of course, for the deuterium content of the ordinary water used as a standard of density. It is assumed (1) that the molecular weights of C_6H_6 and C_6D_6 are 78.11 and 84.14 respectively, (2) that the density of D_2O is $d_{25}^{25} = 1.1074$, and (3) that the atomic percentage of deuterium in the diluent benzene, which was shown to be exactly the same as in the standard water, is 0.015%. The density determinations are accurate to 1 in 10^6 , so that, allowing for the 80-fold dilution, the whole analysis should be correct to 0.1%.

Mechanism of the Exchange.—We have already expressed our views on this subject (*Nature*, 1934, 134, 847), and need only remark that our theory, which regards the exchange as an electrophilic substitution proceeding by attack at a single carbon atom, just as in ordinary aromatic substitution :



is consistent with all that we have discovered to date concerning the deuteration of substituted benzenes by sulphuric acid and similar reagents. This work will be published shortly. Horvut and Polanyi have suggested a mechanism based on a two-point addition involving a Kekulé double bond, and have adduced as lateral evidence hydrogen exchange between sulphuric acid and ethylene (*Nature*, 1934, 134, 847). We can off-set this by showing, for what such evidence is worth, that even paraffins undergo hydrogen exchange with sulphuric acid. This, however, is another section of our work which is not yet ready for publication in detail.

There was never any possibility that the mechanism could consist in successive sulphonation and desulphonation, for it is common knowledge (and we have confirmed the fact) that benzenesulphonic acid is not desulphonated under the conditions of the exchanges. However, as this suggestion has been made more than once by others, we have carried out the following isotopic indicator test. It was first shown that when 55 mols. % aqueous sulphuric acid containing about 2% of deuterium was shaken with ordinary benzene, the proportion of acidic hydrogen to benzenoid hydrogen being 3 : 1, equilibrium in exchange was fully established in 4 days, 9% of the benzene being simultaneously sulphonated. The experiment was then exactly repeated except that "light" aqueous sulphuric acid (*i.e.*, acid of the normal deuterium content) was used, in conjunction as before with "light" benzene, and that a small amount of benzenesulphonic acid was introduced which had been prepared by direct sulphonation of "heavy" benzene. This sulphonic acid contained 25.7 atoms % of deuterium in the hydrogen of the phenyl group, but was normalised with respect to the hydrogen isotopes in the sulphonic acid group. Were benzenesulphonic acid an intermediate in the exchange, the hydrogen of the equilibrium benzene should have contained 0.76% of deuterium, and the water obtained by combustion of the benzene should have been more dense by 800 parts per million than ordinary water. Actually, the density was identical with that of ordinary water to within 1 part per million, which is the error of measurement. It was verified that 8% of benzene had undergone sulphonation just as in the blank experiment. This proves conclusively that the desulphonation of benzenesulphonic acid has nothing to do with the exchange, and that any benzenesulphonic acid formed during this process simply represents so much material put out of action, just as we have always maintained. We foresaw, of course, that the nuclear hydrogen of benzenesulphonic acid would not directly exchange with the hydrogen of the aqueous sulphuric acid; this follows from the known deactivation of the aromatic nucleus towards electrophilic reagents by the sulphonic acid substituent.

Physical Properties of Hexadeuterobenzene.—As we have previously reported, the m. p. of hexadeuterobenzene is 6.8°, *i.e.*, 1.3° higher than that of benzene, and the b. p. is 79.3°,

i.e., 0.8° lower than the b. p. of benzene. A more exact value for the b. p. follows from the vapour-pressure measurement described below : the difference of b. p. at normal pressure is - 0.834°, so that if we standardise on Zmaczynski's value, 80.112°, for the b. p. of benzene (*J. Chim. physique*, 1930, **27**, 503), the b. p. of hexadeuterobenzene becomes 79.288°.

The density of hexadeuterobenzene is $d_{25}^{25} 0.9456$ or $d_4^{25} 0.9429$, and these values may be compared with the benzene densities : $d_{25}^{25} 0.8760$, $d_4^{25} 0.8735$. We should explain, however, that the figures for hexadeuterobenzene are corrected for residual protium, and that the highest density that we have actually measured was that of a sample containing 99.8 atoms % of deuterium which had $d_{25}^{25} 0.94543$. The densities of several less highly deuterated samples are recorded in Table I (p. 920). All these densities were measured with a 1-c.c. pycnometer and should be accurate to the number of figures quoted. For the molecular volume at 25° we have :

$$V^{25}(\text{C}_6\text{H}_6) = 78.11/0.8735 = 89.42 \text{ c.c.}; \quad V^{25}(\text{C}_6\text{D}_6) = 84.14/0.9429 = 89.23 \text{ c.c.}$$

The contraction of 0.21 % observed on passing from benzene to hexadeuterobenzene may be ascribed to the smaller amplitude of the zero-point vibrations of the deuterium compound.

The refractive index of hexadeuterobenzene was measured differentially against that of benzene by using a Pulfrich refractometer with a divided cell. The differences, which were read on the drum of the instrument, should be accurate to the fifth place of decimals, although the absolute values are not reliable beyond the fourth place. For benzene we find $n_D^{22} 1.49982$, and for hexadeuterobenzene $n_D^{22} 1.49779$, the latter value being corrected for residual protium. The refractions and dispersions of a number of specimens of known deuterium content will be found in Table I. For the molecular refractions we have

$$[R_L]_D^{22}(\text{C}_6\text{H}_6) = 26.290 \text{ c.c.}; \quad [R_L]_D^{22}(\text{C}_6\text{D}_6) = 26.146 \text{ c.c.}$$

These values require a slight correction inasmuch as the densities at 25° have been inserted into the Lorentz formula instead of the densities at 22°; our object, however, is to compare the polarisabilities of the isotopic molecules, and for this purpose the correction is not of significance. It will be seen that the optical polarisability (D-light) diminishes by 0.55 % on passing from benzene to hexadeuterobenzene. This is a remarkably large change, as one can appreciate by reflecting that the difference of refractive index between "light" and "heavy" benzene is approximately minus one-half of the difference between benzene and toluene (the differences from benzene are in opposite directions).

In order to obtain the polarisabilities in a static field, we must correct to zero frequency. For benzene we find $n_{5461}^{22} - n_{5790}^{22} = 0.003195$, and for hexadeuterobenzene $n_{5461}^{22} - n_{5790}^{22} = 0.003146$, these figures being subject to an uncertainty of about 3 units in the last decimal place. Using Helmholtz and Ketteler's formula, we obtain

$$[R_L]_{\infty}^{22}(\text{C}_6\text{H}_6) = 25.928 \text{ c.c.}; \quad [R_L]_{\infty}^{22}(\text{C}_6\text{D}_6) = 25.501 \text{ c.c.}$$

These figures show that the static polarisability is 0.50 % smaller in hexadeuterobenzene than in benzene.

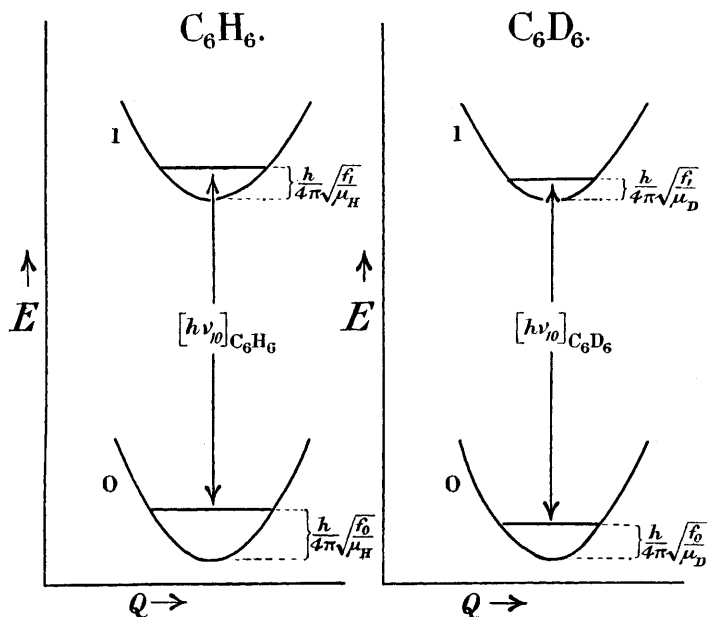
Having regard to the identity of isotopes with respect to nuclear charge, it seems curious at first sight that an isotopic substitution should influence electronic polarisability, but once again we may trace the observed effect to the existence of zero-point energy.

According to the theory of dispersion, the polarisability of a molecule is dependent on what may be described as the "proximity" and "ease of access" of those electronically excited states whose wave functions can be considered to become mixed with the wave function of the ground state when an electric field deforms the normal molecule. The greater the proximity on an energy scale of the excited states to the ground state, and the greater the probability of transitions between the former and the latter, the more will the ground wave function become deformed by admixture with excited wave functions for a given electrical perturbation. The quantitative expression of these ideas is contained in the formula $\alpha_0 = 2 \sum_{j \neq 0} |M_{0j}|^2 / h\nu_{j0}$. Here α_0 is the static polarisability of the normal molecule, $h\nu_{j0}$ is the energy separation of any excited state j from the ground state 0, and $|M_{0j}|^2$ is the measure of the probability of transition between the ground state 0 and the excited state

j ; one sees that α_0 will be great in proportion as the $|M_{0j}|^2$ are great and as the $h\nu_{j0}$ are small. It will frequently happen that a single term of the sum, namely, that related to transitions between the ground level and the lowest electronically excited level ($j = 1$), is much greater than all the others. For the present we shall assume this, and consider only the simplified approximate expression $\alpha_0 = 2|M_{01}|^2/h\nu_{10}$.

It is necessary to consider how $|M_{01}|^2$ and $h\nu_{10}$ behave in consequence of an isotopic substitution. The probability factor $|M_{01}|^2$ is the square of the modulus of an integral (matrix element) involving the electronic wave functions of the ground state 0 and of the excited state 1. If we make the usual assumption that the wave functions, ψ_0 and ψ_1 , are dependent only on the equilibrium positions of the nuclei, despite the fact that the nuclei are really moving with their zero-point energy, then neither the ground wave function, ψ_0 , nor the excited wave function ψ_1 will be altered by isotopic substitution. It follows that the probability $|M_{01}|^2$ will also remain invariant.

FIG. 2.



Effect of zero-point energy on energy of electron transitions.

The energy interval $h\nu_{10}$, on the other hand, will vary with isotopic substitution on account of the nuclear zero-point energy. For any particular electronic state of a given molecule, the zero-point energy will be the sum of a number of terms of the form $\frac{1}{2}h\nu_{\text{vib.}}$, one belonging to each normal vibration. The zero-point energy of benzene will consist of 30 such terms, since the molecule has this number of degrees of vibrational freedom. Let us consider a single term. For small vibrations, the frequency $\nu_{\text{vib.}}$ is given by $(1/2\pi)\sqrt{f/\mu}$, where f is the force-constant and μ the mass-factor ("reduced mass") appropriate to the vibration; so that, except for a constant factor, the zero-point energy term is given by $\sqrt{f/\mu}$. When we pass from benzene to hexadeuterobenzene in the same electronic state the force-constant will remain essentially unchanged whilst the mass-factor will be increased; hence the zero-point energy term will be decreased. When we carry either compound from the ground state to the excited state, the mass-factor of the vibration will remain substantially the same but the force-constant will be reduced; again the zero-point energy term will be decreased. The net effect of these changes can be understood from Fig. 2. The four curves represent the variation with displacement in the vibration (*i.e.*, with the appropriate normal co-ordinate, Q) of the potential energy, E , of benzene and

hexadeuterobenzene both in the ground state, 0, and the excited state, 1. The four zero-point energy terms depend, as is indicated beside the curves, on a force-constant which varies with the state (f_0 and f_1) and a reduced mass which varies with the compound (μ_H and μ_D). Quite generally, the force and mass-factors will exhibit the inequalities $f_0 > f_1$ and $\mu_D > \mu_H$. It follows that the four zero-point energy terms will cause the energy of transition between the ground and the excited states to be greater in hexadeuterobenzene than in benzene by the positive quantity $(h/4\pi)(f_0^{\frac{1}{2}} - f_1^{\frac{1}{2}})(\mu_H^{-\frac{1}{2}} - \mu_D^{-\frac{1}{2}})$. This is an effect due to only one normal vibration, and the whole difference in the electronic transition energy due to nuclear zero-point energy will be the sum of 30 such terms. Therefore, if benzene were to satisfy our simplifying assumption that only one excited state need be counted for the calculation of the polarisability, then the values of this constant for benzene and hexadeuterobenzene would simply stand in the inverse ratios of the transition energies, the polarisability of hexadeuterobenzene being the smaller.

In Part V we show that benzene has, not one, but three closely situated electronically excited states in the near ultra-violet. However, this does not greatly complicate the position provided that it is still a good approximation to consider only the contributions made by these three states to the sum giving the polarisability, α_0 . The factors by which the energy of transition from each of these excited states to the ground state is greater in hexadeuterobenzene than in benzene are 1.0063, 1.0045, and 1.0046. Hence the three terms which we now consider to be effective in the summation giving the polarisability will be smaller for hexadeuterobenzene than for benzene by 0.63%, 0.45%, and 0.46% respectively. It follows that the polarisability itself will be smaller in hexadeuterobenzene than in benzene by a proportion which is bound to lie within the limits of the individual percentages quoted, and may as an approximation be set equal to their average, *viz.*, 0.51%. The agreement with the observed percentage difference, 0.50%, testifies to the essential truth of the explanation given.

TABLE I.

Density, Refraction, and Dispersion of Deuterated Benzenes.

D, atoms, %.....	0.0	51.6	81.7	92.9	97.4	99.8	100.0
d_{25}^{25}	0.87596	0.91242	0.93447	—	0.94424	0.94543	0.94560
n_D^{22}	1.49982	1.49877	1.49813	1.49795	1.49783	—	1.49779
$(n_{5461}^{22} - n_{5790}^{22}) \times 10^4$...	3195	3167	3158	—	3144	—	3146

Many authors have evinced interest in the vapour pressure of isotopic compounds, and especially in those cases in which the modification having the greater molecular weight has also the greater vapour pressure. Benzene is an example of this, and moreover one of particular interest, inasmuch as the special explanations which have been advanced in other cases (hydrogen fluoride and acetic acid), and which indeed may be substantially true for these, can scarcely be considered to apply to benzene. Evidently some much more general treatment is required, and for this reason Mr. C. R. Bailey and Mr. B. Topley have made a special theoretical study of the matter. Their conclusions, which are described in an Appendix to this paper, furnish both the general principles which should govern the discussion of any normal example and a semi-quantitative treatment of the particular case of benzene. On the experimental side the vapour pressure of hexadeuterobenzene has been measured differentially against that of benzene over the temperature range 0–80°, the liquids being supercooled at the lowest temperatures investigated. The pressure differences should not be in error by more than 0.1 mm.

The measurements were carried out with a differential tensimeter made of tubing of 7 mm. bore and sufficiently uniform to obviate the necessity for any correction due to the capillary depression of the manometric liquid, which was pure, freshly distilled mercury. The glass was carefully out-gassed, and the mercury was boiled out in a vacuum whilst in the tensimeter. The benzene samples were dried with phosphoric oxide, introduced without access of moisture, and further out-gassed in the tensimeter by repeated freezing at -78° in a vacuum, melting, re-freezing and re-exhausting, before sealing off from the gas-line. The tensimeter was wholly immersed in the thermostat, and the observations were taken through a plate-glass window by

means of a cathetometer in the field of which both mercury surfaces were simultaneously visible. The normal precautions were taken as to plumb-lining, and refraction errors were proved to be negligible by observations on a scale placed in the thermostat. As we wished to conserve our purest specimens of hexadeuterobenzene for those investigations for which isotopic purity is most essential, the vapour pressures were measured with a specimen containing 7.1% of residual protium; however, the relation of the order of magnitude of the pressure differences to that of the error of measurement is such that the extrapolation to zero protium content should be safe. The extrapolations are linear and it is immaterial whether one uses the vapour pressures themselves or their logarithms. Young's values for benzene (J., 1889, 55, 486; *Phil. Mag.*, 1887, 661) have been taken as basis for the comparison.

The results, given in Table II, satisfy the equation

$$\log_{10}(p_{C_6H_6}/p_{C_6D_6}) = - (4.585/T) + 0.0018$$

where the p 's are vapour pressures and T is the absolute temperature; this applies throughout the entire range. Zmaczynski's results for the vapour pressure of benzene in the neighbourhood of its b. p. may be expressed by the relation

$$\log_{10}p_{C_6H_6} = - (1671.34/T) + 7.6125$$

the pressures being expressed in mm. of mercury. Hence for hexadeuterobenzene in the neighbourhood of its b. p. we have

$$\log_{10}p_{C_6D_6} = - (1666.76/T) + 7.6107$$

This is the equation from which we calculated the b. p. quoted above. It will be observed that, although the terms dependent respectively on the latent heat and chemical constant are of comparable importance in the equations giving the separate vapour pressures of benzene and hexadeuterobenzene, yet almost the whole of the difference between the two vapour pressures arises from the difference between the corresponding latent heats of evaporation. For the individual molecular latent heats in the neighbourhood of the b. p.'s we find

$$\lambda^{80^\circ}(C_6H_6) = 7639.1 \text{ cal.}; \quad \lambda^{80^\circ}(C_6D_6) = 7618.2 \text{ cal.}$$

For the difference between the latent heats over the whole experimental range 0—80° we have

$$\lambda(C_6H_6) - \lambda(C_6D_6) = 20.96 \text{ cal.}$$

TABLE II.

Vapour Pressures of Benzene and Hexadeuterobenzene.

Temp. (T — 273.1°).	$p_{C_6H_6}$ (mm. Hg).	Δp (obs.).	Δp (corr.).	$p_{C_6D_6}$ (mm. Hg).	Temp. (T — 273.1°).	$p_{C_6H_6}$ (mm. Hg).	Δp (obs.).	Δp (corr.).	$p_{C_6D_6}$ (mm. Hg).
0.0°	26.5	0.9	1.0	27.5	45.0°	220.7	6.0	6.4	227.1
5.0	34.7	1.1	1.2	35.9	50.0	269.0	7.2	7.7	276.7
10.0	45.4	1.4	1.5	46.9	55.0	323.3	8.6	9.2	332.5
15.0	58.2	1.8	1.9	60.1	60.0	388.6	10.0	10.8	399.4
20.0	74.7	2.2	2.4	77.1	65.0	461.2	11.7	12.6	473.8
25.0	94.0	2.7	2.9	96.9	70.0	547.4	13.6	14.6	562.0
30.0	118.2	3.4	3.6	121.8	75.0	642.3	16.0	17.2	659.5
35.0	146.3	4.1	4.4	150.7	80.0	753.6	18.6	20.0	773.6
40.0	181.1	4.9	5.2	186.3					

APPENDIX.

Discussion of the Vapour Pressure of Hexadeuterobenzene.

By C. R. BAILEY and B. TOPLEY.

It is shown in the foregoing paper that the relative vapour pressures of C_6D_6 and C_6H_6 are expressed by $p_{C_6H_6}/p_{C_6D_6} = 1.00415 \exp. (-20.96/RT)$ in the range 0—80°. The slight uncertainty in the two empirical constants is not sufficient to affect the main con-

tude of, though possibly somewhat larger than, the value of kT at ordinary temperatures, and the quantum of the corresponding quasi-periodic motions lies between kT and $0.1kT$.

The whole of the following discussion is based upon the simplifying assumptions concerning the liquid which we now state. The cohesion of the liquid is produced by forces which have the additive character of van der Waals forces, and the molecules are not polymerised by any bonds having the directed and non-additive nature of valency forces. Each molecule is considered to execute its thermal motion separately within the constraints imposed by surrounding molecules, *i.e.*, in a potential hollow which—although in reality fluctuating—is treated as having some constant average form the same for all molecules of a pure substance.

The partition function ratio g'/g for this model of the liquid state can be written as the product of factors

$$g'/g = \{\exp.(\chi - \chi')/kT\} \{g'_{\text{vib.}}/g_{\text{vib.}}\} \{g'_o/g_o\} \{g'_h/g_h\} \dots \quad (3)$$

χ, χ' are the potential energies of the C_6H_6 and C_6D_6 molecules in the liquid measured from the lowest energy states in the gas as arbitrary zeros. For the purpose of this definition, the molecules are considered as rigid structures, and χ, χ' are measured down to the potential minimum of each of the six co-ordinates defining the potential hollows; the zero-point energies of the thermal motions of the molecules as rigid structures are taken into account in the partition function ratios g'_o/g_o and g'_h/g_h .

The ratio $g'_{\text{vib.}}/g_{\text{vib.}}$ corresponds to the reciprocal of $f_{\text{vib.}}/f'_{\text{vib.}}$ for the gas phases. The ratio g'_o/g_o contains the partition functions for the three degrees of freedom involving lateral motion of the centre of gravity of the molecule, *i.e.*, for the degrees of freedom which replace the free translation in the gas; similarly g'_h/g_h contains the partition functions for the three-dimensional hindered rotation (rotation-oscillation) replacing the free rotation in the gas.

Each of the four factors in equation (3) proves to be important in determining the numerical value of g'/g . We have examined the contribution of each to the vapour-pressure ratio by expressing the factor in the form $A \exp. (B/RT)$, where T is the absolute temperature, R the gas constant in cal. per mol., and A and B are empirically chosen to reproduce as closely as possible the numerical behaviour of the factor in question over the temperature range for which the vapour-pressure data have been determined. We thus obtain

$$p_{C_6H_6}/p_{C_6D_6} = \Pi A. \exp. \Sigma B/RT \dots \quad (1a)$$

the product Π and the sum Σ extending over the three factors of equation (2) and the four factors of equation (3).

The last two factors in equation (2) provide only an "A" factor of 0.672. It is convenient to deal with the first factor $f_{\text{vib.}}/f'_{\text{vib.}}$ along with $g'_{\text{vib.}}/g_{\text{vib.}}$. There is, in general, a small shift in the internal vibration frequencies when a vapour condenses, and a corresponding change in the internal zero-point energy of the molecule (Buchheim, *Physikal. Z.*, 1935, **36**, 694; Mecke and Vierling, *Z. Physik*, 1935, **96**, 559). This shift is nearly always in the sense that $\nu_{\text{gas}} - \nu_{\text{liquid}}$ is positive. In the particular case of benzene the effect has been measured in the infra-red for a number of bands, including fundamentals, overtones, and combination tones, by McAlister and Unger (*Physical Rev.*, 1930, **36**, 1799), Silvermann (*ibid.*, 1932, **41**, 486), Leberknight (*ibid.*, 1933, **43**, 971), Barnes (*ibid.*, 1930, **36**, 296) and Dreisch (*Z. Physik*, 1924, **30**, 200). In eleven different observations the shift is in the usual direction, but in one exception a shift in the opposite direction, several times larger than any of the normal shifts for unpolymerised substances, is recorded by Dreisch (*loc. cit.*). Attributing this to error, we have omitted it. The recorded differences $\nu_{\text{gas}} - \nu_{\text{liquid}}$, when converted into fractional differences $1 - \nu_{\text{liquid}}/\nu_{\text{gas}}$, range from 0.00148 to 0.00475 with an average of 0.00280. It is a safe assumption that in hexadeuterobenzene the corresponding vibrations will show essentially the same fractional shifts. The further assumption which we are compelled to make, *viz.*, that the fractional shift averaged over the 30 normal modes of vibration may be taken as 0.0028, is also not likely to be seriously in error.

We are concerned only with the quantity

$$\{f_{\text{vib.}}/f'_{\text{vib.}}\} \{g'_{\text{vib.}}/g_{\text{vib.}}\} = \{f_{\text{vib.}}/g_{\text{vib.}}\} \{g'_{\text{vib.}}/f'_{\text{vib.}}\}.$$

In the temperature range in question, the factors of the form $(1 - \exp. h\nu/kT)$ can be omitted, leaving a product of 30 factors of the form $\exp.[0.0028h(\nu' - \nu)/2kT]$. Inserting into this product the frequencies of benzene and hexadeuterobenzene and the degeneracies (see Part VIII), we obtain a "B" term of -32 cal. per mol.

The energy difference $\chi - \chi'$ in equation (3) differs from zero in so far as the van der Waals forces are not identical for the isotopic molecules. To estimate the difference for benzene and hexadeuterobenzene we utilise the theory of London (*Z. physikal. Chem.*, 1930, *B*, **11**, 222). The approximations in the theory are considerable, but the successful calculation of the absolute heat of sublimation of solid benzene by de Boer (*Trans. Faraday Soc.*, 1936, **32**, 10) and of quinone by Wassermann (this vol., p. 432) justifies empirically our use of it here. Instead of the relationship between the van der Waals forces and polarisability given by London, we use the approximation given by Slater and Kirkwood (*Physical Rev.*, 1931, **37**, 682) for the mutual energy between them. Treating, as de Boer does, the CH groups as though their electronic distribution were spherically symmetrical, and assuming that the average arrangement of the CD groups in the *liquid* is the same as the average arrangement of the CH groups except that all distances are contracted slightly, then the difference between the isotopic molecules reduces to the expression $\chi'/\chi = (\alpha'/\alpha)^{3/2}(V/V')^2$, where α and V are respectively the polarisability and the molecular volume. Since $\alpha' = 0.995\alpha$ and $V' = 0.9979V$ at ordinary temperatures and we may assume these ratios to hold between 0° and 80° , we have for χ'/χ the value 0.99667. Identifying $-\chi$ with the latent heat of evaporation of benzene (5.2×10^{-13} erg per molecule), we find $\chi - \chi' = -1.7 \times 10^{-15}$ erg per molecule, giving us a "B" term of -25 cal. per mol. Inserting in equation (1a) the partition ratios which have been evaluated above, we have

$$\dot{p}_{C_6H_6}/\dot{p}_{C_6D_6} = 0.672 \exp. (-57/RT) \{g'_o/g_o\} \{g'_h/g_h\} \dots \quad (1b)$$

The factor 0.672 cannot be in error by more than 1—2%, and there is no reason to believe that the exponent $(-57/RT)$ can be as far out as, say, 30%. Comparing equation (1b) with equation (1), we see that the partition function ratios concerned with the six degrees of freedom of motion of the molecule as a whole in the liquid phase must be capable of being expressed formally by

$$\{g'_o/g_o\} \{g'_h/g_h\} = A \exp. B/RT$$

with $A = 1.00415/0.672 = 1.49$ and B a positive quantity equal to the difference $(57 - 20.96)$ but with a toleration of say ± 14 cal.

We have no means of determining *a priori* the best form of potential function to represent the restriction upon the motion of the molecule in these six degrees of freedom. In any case the six zero-point energy differences must exist and must contribute a "B" term of the required sign. There remains the question whether, with a reasonable choice of potential function or functions, an "A" factor of the required size could be reconciled with a "B" term lying within the limits given. We have studied the numerical behaviour of the partition ratios for three simple potentials:

(1) $E_{\text{pot.}} = \frac{1}{2}Kx^2$, where x is the displacement of the centre of gravity from its equilibrium position. For this harmonic oscillator we have taken the same force constant K for both benzene and hexadeuterobenzene; our final conclusion (a qualitative one) would not be altered by using slightly differing force constants. From symmetry, we should expect that two only of the three degrees of freedom included in g'_o/g_o will have the same K . The rotation-oscillation will also have the form of partition function associated with simple harmonic motion if we substitute for x the angular displacement round a principal axis, and for the mass of the molecule the moment of inertia round the same axis; again two only of the degrees of freedom will have the same force constant.

(2) $E_{\text{pot.}} = \frac{1}{2}K_1x^2 - K_2x^4$; the force constants K_1 and K_2 being chosen so that $\delta E_{\text{pot.}}/\delta x$ is reduced to zero at a value of x equal to one-half the distance between the centres of adjacent molecules of benzene, and $E_{\text{pot.}}$ is 1350 cal. per mol. at this point, in conformity with the viscosity data (see p. 922, footnote). It is clearly no objection that this potential is not periodic in x . The energy levels given by a first-order perturbation calculation are well-known (Pauling and Wilson, "Introduction to Quantum Mechanics," 1935).

(3) A potential hollow in the form of a box in which $E_{\text{pot.}} = \text{constant}$ for $-x_0 < x < x_0$, and $= \infty$ at $-x_0$ and x_0 , *i.e.*, the molecule moves a short distance at constant potential energy $E_{\text{pot.}}$, and is then "reflected" from a potential wall. We have arbitrarily taken x_0 to be one-tenth of the distance between the centres of adjacent molecules. The energy levels are those of a mass point moving in a similar potential with the same free path between reflections. A similar potential wall can be imagined to limit the angle co-ordinates of the rotational motion.

For each of these potentials we have evaluated the partition functions $g_o = \Sigma \exp(-E_n/kT)$ and $g'_o = \Sigma \exp(-E'_n/kT)$ at 0° , 40° , and 80° and—in the case of the harmonic oscillator—for a range of frequencies. The partition function for the perturbed oscillator proved to be very similar to that of the harmonic oscillator. The empirical constants were then found by which the temperature dependence of the ratios g'_o/g_o and similarly for g'_n/g_n can be expressed as nearly as possible in the form $A \exp(B/RT)$.

The results of these detailed calculations can be summarised as follows: in all three forms of potential function, $A > 1$ and $B > 0$ as we require. We find, however, that the conditions imposed on the quantity $\{g'_o/g_o\}\{g'_n/g_n\}$ are not sufficiently rigorous because of the estimated uncertainty of ± 14 cal. in the "B" term. In fact, the conditions in question can be satisfied by many combinations of quite reasonable assumptions about the thermal motions of the molecules in the liquid. Accordingly, we cannot work backwards from the observed vapour pressures to draw any definite conclusion of a quantitative nature about the potential hollow. On the other hand, the parabolic potential and the potential "box" do not differ drastically in the consequences they entail for the ratio $p_{\text{C}_6\text{H}_6}/p_{\text{C}_6\text{D}_6}$, and we are led to the conclusion that any acceptable form of potential would predict a temperature-independent factor for the vapour pressure ratio of 0.8—1.1, on the basis of the ± 14 cal. uncertainty in the exponent. Even apart from this rather large uncertainty, we find that there would still remain a considerable uncertainty in the temperature-independent factor; however, in principle, the uncertainty in the exponent could be reduced by more exact and complete knowledge of the refractivities and the shifts in the infra-red absorption and the Raman scattering frequencies on passing from the vapour to the liquid.

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