

Electrification was avoided by keeping all movements of the float slow, and its absence was shown by the constancy of the set point for pure carbon tetrachloride after repeated distillation; the same considerations apply to the influence of dissolved air. The greatest care was taken to avoid contamination, decomposition of the tetrachloride by particles of phosphorus pentoxide at the boiling point and by hot glass. Ground joints were used, and all apparatus was cleaned by acid potassium permanganate.

It is clear that no isotopic separation occurs on distillation, using an efficient column, as found by Grimm<sup>3</sup> to 1 in  $10^5$ . About 30 gm. of pure carbon tetrachloride was refluxed with excess sodium amalgam for some hours, until about half of the tetrachloride was decomposed. On distilling the residue at 77°, the density of the product was  $6 \times 10^{-5}$  greater than that of the original carbon tetrachloride, but this difference was rapidly reduced to a constant value of  $(6 \pm 0.5) \times 10^{-6}$  after repeated fractionation. Hence the reaction is not entirely quantitative, but the impurity must have a boiling point differing greatly from that of tetrachloride. The residual difference in density is probably due to isotopic separation. A repetition of the whole experiment with about one third decomposition gave a density change of  $(4 \pm 0.5) \times 10^{-6}$ . Repeated readings were made on the set points.

The molecular species  $C^{35}Cl_4$ ,  $C^{35}Cl_3^{37}Cl$ ,  $C^{35}Cl_2^{37}Cl_2$ ,  $C^{35}Cl^{37}Cl_3$ , and  $C^{37}Cl_4$  are present according to the binomial frequency distribution  $(\frac{1}{4} + \frac{3}{4})^4 \times 100$  to the extent of 31.6, 42.2, 21.1, 4.7 and 0.4 per cent, with 25 per cent  $^{37}Cl$  and 75 per cent  $^{35}Cl$ . Moreover, density will be very nearly proportional to molecular weight (this holds to within 0.4 per cent for  $H_2O$  and  $D_2O$ ). Hence the density of the various molecular species can be calculated from that of the mixture, assuming additivity of volumes. It can be shown that for a small increase in percentage of Cl equal to  $\alpha$ ,  $100/D - 100/D' = -\alpha[-4q^3/d + 4(q^3 - 3q^2p)140/142d + 6(2q^2p - 2qp^2)140/144d + 4(3qp^2 - p^3)140/146d + 4p^3 140/148d]$ , where  $p = \frac{1}{4}$ ,  $q = \frac{3}{4}$  and  $d$ ,  $D$  and  $D'$  are the densities of  $C^{35}Cl_4$ , and the initial and changed mixture. Hence  $\alpha = 7.3 \times 10^3(D' - D)d/D^2$  and from the above change in density,  $6 \times 10^{-6}$ ,  $\alpha = 3 \times 10^{-3}$ , or ratio of percentage of  $^{37}Cl$  in the heavy and light tetrachloride is  $1 + 1.3 \times 10^{-3}$ . The percentage of  $^{13}C$  is too small to enter into consideration.

Probably the separation proceeds because of a difference in activation energies, which has the advantage over 'physical' methods of introducing an exponential factor. Activation of the tetrachloride probably involves transition to a polar state similar to that conceived by Ogg and Polanyi<sup>4</sup>, who observe a parallelism between activation and bond energy. Variation in the latter may be roughly calculated<sup>5</sup> from the Raman frequencies, the symmetrical mode giving  $\Delta\nu = 3.15 \text{ cm}^{-1}$ , which gives a difference in zero point energies of about 5 cal. per gm. mol. for  $C^{35}Cl_4$  and  $C^{35}Cl_3^{37}Cl$ .

The separation, although small, is large relative to that produced by repeated fractionation, and on an industrial scale is capable of yielding much greater separations.

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<sup>1</sup> Fetkenheuer, *Z. anorg. Chem.*, **117**, 281 (1921).

<sup>2</sup> Sligh, *J. Amer. Chem. Soc.*, **42**, 60 (1920).

<sup>3</sup> *Z. phys. Chem.*, **B**, **2**, 181 (1929).

<sup>4</sup> *Trans. Faraday Soc.*, **31**, 1375 (1935).

<sup>5</sup> Langseth, *Z. Phys.*, **72**, 350 (1931).

### Chemical Reaction in Ionised Gases

It is frequently assumed that the chemical reactions which take place in ionised gases are reactions in which one or more of the reacting atoms or molecules react whilst ionised. Many years ago Kirkby adduced evidence, which still remains strong in our opinion, that this could not be the case for discharges through electrolytic gas<sup>1</sup>. The necessity for a reaction mechanism involving ions has also been questioned more recently by H. S. Taylor<sup>2</sup>, and in at least one other important paper a contrary view has been considered favourably<sup>3</sup>.

For some years we have been examining the kinetics of reactions in discharges; we hope to publish our conclusions in detail very soon. In the course of this work, we have found scarcely any reaction which cannot be accounted for qualitatively to our satisfaction on the assumption that the reacting particles are all *neutral*. One reacting particle is usually one of the main atoms or molecules present independently of the passage of the current, and the other a neutral atom or molecule or molecular fragment, in a normal or excited state, produced by electron collision with one of the main atoms or molecules. In other words, the reactions appear to be related to the conductivity of the gas only incidentally, in the same way as a great part of the luminosity of the discharge. In those cases where all the relevant data are known with sufficient accuracy (unfortunately these are few), the observed reaction rate agrees closely with that predicted on the excitation hypothesis.

Although we have not yet considered so fully the reactions initiated by  $\alpha$ -particles and fast electrons, we believe (with Krüger<sup>4</sup>) that these are likewise mainly reactions involving neutral particles only.

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<sup>1</sup> Kirkby, *Proc. Roy. Soc. A*, **85**, 151 (1911)

<sup>2</sup> *J. Amer. Chem. Soc.*, **52**, 1121 (1930).

<sup>3</sup> Linder, *Phys. Rev.*, **35**, 679 (1931).

<sup>4</sup> *Ann. Physik.*, **78**, 113 (1925).

### Carcinogenic Activity and Substantivity

The significant work of J. W. Cook and his collaborators<sup>1</sup> on the relation between the structure and carcinogenic activity of the higher aromatic hydrocarbons prompts the observation that a similar type of relation holds between the structure of an anthraquinone derivative and the affinity of its leuco-form for textile fibres. With few exceptions, Cook *et al.* have found that, of the hydrocarbons related to anthracene, those derived by attachment of alkyl groups or hydrocarbon rings to the 1:2- or 1:2:5:6-positions possessed carcinogenic activity, whilst other orientations were inert.

The same angular orientation of fused rings appears to be equally significant in determining the dyeing properties of anthraquinone derivatives. Whilst 1:2-benzanthraquinone is a feeble vat dye, neither anthraquinone nor naphthacenequinone has affinity. The same relation appears to hold for the heterocyclic