$$K = \frac{c.\,l_s/l_w\ .\ p^3}{(1-p)^2\ .\ S_v^2} = \frac{l_s/l_w\ .\ p^3\ .\ d^2{}_w}{(1-p)^2\ .\ 36},$$

where p is the porosity, S_v the specific surface per c.c., $c.\ l_s/l_w$ a constant dependent upon the shape of the capillaries, and d_w is what Kozeny calls the "effective diameter", and what we call the "volume-surface diameter", which he calculates as

$$1/d_w = \int dG/d_i,$$

where G is the weight of the grain mixture (p. 305, ref. 4), taken as unity.

Thus, Kozeny calculates d_w as the harmonic mean of the weight distribution.

Since

$$\frac{1}{d_w} = \Sigma\frac{1}{d_i}\frac{dG}{G} = \frac{\rho\,\Sigma\frac{1}{d_i}d_i{}^3n_i}{\rho\,\Sigma d_i{}^3n_i} = \frac{\Sigma d_i{}^2n_i}{\Sigma d_i{}^3n_i} = \frac{1}{M_{vs}},$$

where ρ is the density, d_w equals the volume-surface mean of the Kozeny equation. But, except for the case of a monodisperse aggregate—where we cannot speak of an average at all—the quantity d_w in the equation for the permeability constant as the volume-surface diameter of the structure $\Sigma d_i{}^3n_i/\Sigma d_i{}^2n_i$ can differ considerably from the harmonic mean of the number distribution.

That Kozeny was not aware of the distinction between the two averages, and really worked with the number harmonic mean instead of with the volume-surface diameter, can be seen from his table on p. 306 (ref. 4). He there calculates $1/d_w$ for the class intervals of particle-size according to the formula for the number harmonic mean, as the observed value with which to compare the theoretical value of $1/d_w$ obtained from his equation (36), where d_w has the same structure as in the fundamental equation for the permeability constant.

That there is not more discrepancy between the two sets of values for d_w is due to the fact that the size intervals are so small as to approximate to monodisperse aggregates. In the case of a polydisperse aggregate, the substitution of d_w calculated as the harmonic mean into the formula for the permeability constant, where d_w appears to the second power, could lead to very wrong results.

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Bis-Ethylene-Dichloroplatinum

Zeise's salt, $K[C_2H_4PtCl_3]$, has been known since 1830[1], and dichloro-*bis*-ethylene-μμ′-dichlorodiplatinum, 'ethylene platinous chloride' $(C_2H_4PtCl_2)_2$, was characterized by Anderson[2] in 1934; but attempts to prepare *bis*-ethylene-dichloroplatinum, $(C_2H_4)_2PtCl_2$, have hitherto been unsuccessful[3,4]. Anderson[4] has, however, reported slight evidence, which was rejected by Hel'man, for a simple *bis* styrene complex.

In this respect, olefine platinous chloride complexes are exceptional, for in every other case of the co-ordination of a neutral ligand to platinous chloride the non-ionic complex, L_2PtCl_2, is known (L = ligand), and when the ionic or bridged complexes are also known, these are as a rule less stable. Notable exceptions to this second generalization are the complexes where $L = PF_3$ and $L = CO$. Both of these readily decompose thermally at 100–150° C. with loss of the ligand to produce the very stable bridged complexes:

$$2L_2PtCl_2 \rightleftharpoons (LPtCl_2)_2 + 2L.$$

We now find that olefine complexes are extremes of this latter type. When ethylene was passed through a strong solution of ethylene platinous chloride in dry acetone or methylethylketone cooled to −70° C., a canary-yellow crystalline solid of the composition $(C_2H_4)_2PtCl_2$ separated. It was almost insoluble in the ketone at −70° C. but dissolved to give a yellow solution when the reaction mixture was allowed to warm to above −50° C. From Hel'man's work on substitution in the olefinic platinous complex series, this yellow complex would be given a *trans* configuration, and its instability can be explained as the sum of the rather weak co-ordinating affinity of ethylene, together with the strong labilizing effect of an ethylene molecule on the group in the *trans* position to itself.

The yellow $(C_2H_4)_2PtCl_2$ is very unstable, and on slowly warming to about −10° C. in an ethylene atmosphere it starts to revert to the orange $(C_2H_4PtCl_2)_2$, then on cooling again it is reconverted, at least on the surface, to the yellow $(C_2H_4)_2PtCl_2$. Even at −70° C. the second molecule of ethylene may be driven from a suspension of the yellow solid in acetone by passage of carbon dioxide, when the suspension dissolves gradually and completely in the form of $(C_2H_4PtCl_2)_2$.

Solid ethylene platinous chloride shows no evidence of combination with either liquid or gaseous ethylene at low temperatures, and the ketone appears to facilitate the reaction by opening up the bridge; in confirmation, we have found that ethylene platinous chloride has a molecular weight corresponding to $(C_2H_4PtCl_2)$, and not the dimer in boiling acetone solution.

A second solid of exact composition $(C_2H_4)_2PtCl_2$ + 10·75 per cent Pt which effervesces at once with potassium cyanide solution in the manner characteristic of ethylene platinous complexes has been obtained in very small quantities as a minor product of the reaction of tri-*n*-propylphosphine (2 mol.) on ethylene platinous chloride (1 mol.) in acetone solution at −70° C. It separates slowly after the reaction mixture has warmed to room temperature and is an 'off-white' amorphous-looking solid which is insoluble in all solvents tried and blackens at 150–160° C. This may be *cis*-$(C_2H_4)_2PtCl_2$, but it could be a polymeric substance.

One of us[5] has recently reviewed critically the structures proposed for olefine complexes and, with the exception of Hel'man's structure[6], based on the apparently established fact that simple non-ionic olefine platinous complexes do not exist, most of these could be rejected and the remainder shown to be improbable. Hel'man's structure, in the terms in which she conceives it, may now be rejected; but the existence of *bis*-ethylenedichloroplatinum does not vitiate the view that *d*-orbitals may be involved in olefine co-ordination.

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Pyrolysis of 1.2 Dichlorethane

THE kinetics of the pyrolysis of 1.2 dichlorethane have recently been described by Barton and Howlett[1]. Over the temperature-range 360°–480° C. they find that the reaction is first order and proceeds by a radical chain-mechanism in vessels coated with a carbonaceous film ($k = 10^{10 \cdot 81} \exp -47{,}000/RT$). Strong evidence for the radical nature of the decomposition is provided by the powerful inhibiting effect of propylene. The maximally inhibited rate, which is independent of further increase in propylene concentration, is shown to be partially heterogeneous in character.

Almost simultaneously, Baldt and Cremer[2] have published an account of a similar investigation which led to different conclusions. They claim that the graph of log k against $1/T$ is sharply segmented corresponding to a heterogeneous reaction ($k = 10^{4 \cdot 15} \exp - 28{,}100/RT$) from 377° to 415° C., and from 415° to 442° C. to a unimolecular process ($k = 10^{15 \cdot 70} \exp -64{,}500/RT$). (The graph does not, in fact, correspond to the data quoted in a table. Accepting the latter, the activation energy for the heterogeneous process becomes $\sim$ 25,500 cal./gm. mol.)

This result does not, in fact, follow from the Arrhenius plot, for it is easily seen that neither of these two reaction-rates is negligible in comparison with the other at any point of the narrow temperature-range studied. Thus the operation of these two reactions would lead to a continuous curve for the Arrhenius plot, and furthermore the value of log k at 415° should be 0·3 units above the point of intersection of the limiting straight lines, because the observed velocity constant would be the sum of the two (equal) constants for the alternative reactions. (This assumes that reaction does not greatly disturb the equilibrium between normal and activated molecules.) However, the experimental points lie on excellent straight lines with a point actually at the intersection. This is difficult to interpret.

It is noteworthy that at 442° C. (where direct comparison is possible) the rate constant quoted by Baldt and Cremer is intermediate between the values given by Barton and Howlett for the normal and maximally inhibited reactions. Coupled with the fact that the pyrolysis is notoriously sensitive to trace contaminants[3], this suggests that Baldt and Cremer may have been observing partially retarded decompositions. The latter give the impression that their rates are obtained for reactions in clean glass vessels, but it is most probable that they refer to product-fouled surfaces. Thus their rates are slower than those of Barton and Howlett, who report the accelerating effect of clean glass surfaces[4].

The question of the nature of 1.2 dichlorethane decomposition is an important one. The fact that it proceeds by a radical mechanism, whereas 1.1 dichlorethane decomposes unimolecularly, is strong evidence for the predictions put forward correlating structure and mode of decomposition in chlorohydrocarbon pyrolyses by Barton, Onyon and Howlett[5]. Experiment has so far verified these predictions[6].

A significant difference between the two experimental techniques lies in the method of pressure measurement used to follow reactions. Barton and Howlett used an all-glass Bourdon gauge, whereas the other authors employed a heated mercury capillary manometer. Mercury is known to inhibit the analogous decomposition of ethyl bromide[7], and would be expected to react with chlorine atoms under the experimental conditions, thus suppressing any tendency towards radical mechanisms.

I have therefore carried out further experiments in a new apparatus, using an all-glass pressure-measuring system to follow the reaction. In addition, a heated 1-mm. capillary tube containing mercury could be connected to the reactor, or isolated by a tap, so that decompositions in the presence or absence of mercury could be studied at will. General experimental procedure was as described previously[1].

In the absence of mercury, the new experiments have amply confirmed the results of Barton and Howlett for both clean and coated vessels. Furthermore, mercury vapour has been shown to inhibit the reaction. The runs were carried out using the mercury capillary heated to 120° C., at which the vapour pressure of mercury is approximately 0·8 mm. Actual determination of the rise in pressure on opening the evacuated reactor to the capillary gave a value of 0·5 mm. The results obtained in a coated vessel are summarized in the accompanying table.

Temp.	$(CH_2Cl)_2$ alone			$(CH_2Cl)_2$ + Hg	
	No. of runs	$10^4 \times$ mean k	$10^4\,k$ (B. and H.) (ref. 1)	No. of runs	$10^4 \times$ mean k
435° C.	3	1·71	1·99	4	1·31
447° C.	9	3·53	3·46	7	2·55
459° C.	3	6·49	6·57	3	5·47

All rates are expressed in units $sec.^{-1}$.

The first day's experiments with a clean 'Pyrex' reactor gave a mean $k = 3 \cdot 3 \times 10^{-3}$ $sec.^{-1}$ at 408° C., in good agreement with the dynamic results of Barton[3].

The retardation of the homogeneous pyrolysis by traces of mercury vapour provides further evidence of the radical nature of the decomposition, and it must be concluded that the results of Baldt and Cremer refer to partially inhibited reactions.

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