decomposition in paraffin solution between 135° and 175°. The Arrhenius equation $k = Ze^{-E/RT}$ proved to be valid.

	Z	E
Bimolecular Association	1.2×10^6 1/gm.-mol. sec.	16·4 kgm. cal.
Monomolecular Decomposition	6×10^{12} sec.$^{-1}$	34 kgm. cal.

The association is 'slow' because the value of Z is much smaller than the collision frequency in the gas phase (about 10^{11}). This cannot be connected with a restricted probability of electron transition because the Z value of the decomposition reaction is almost normal[1]. This indicates that the slowness of the formation of *dicyclo*pentadiene is best explained by a statistical mechanical treatment of entropy change[2].

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[1] Wigner and Polanyi, *Z. phys. Chem.*, **139**, 439 (1928).
[2] Eyring, *J. Chem. Physics*, **3**, 107 (1935) and subsequent publications. Evans and Polanyi, *Trans. Farad. Soc.*, **31**, 875 (1935). Cf. also Rodebush, *J. chem. Phys.*, **1**, 440 (1933); Rice and Gershinowitz, ibid., **2**, 853 (1934).

Collision Frequency in Solution; Kinetics of Diene Syntheses in Solution and in the Gaseous State

In the Arrhenius equation

$$k = Ze^{-E/RT} = PCe^{-E/RT},$$

C is the collision frequency and P the 'steric factor'. For gas reactions the kinetic theory gives $C \sim 10^{11}$. Bimolecular reactions in solution can be divided into two main types[1] : (a) reactions involving simple ions where $Z \sim 10^{11}$; (b) reactions involving molecules with many internal degrees of freedom, where $Z \ll 10^{11}$ ('slow reactions'). For reactions (a) a statistical mechanical treatment shows[2] that P should be of order unity and here it can be concluded that C is of order 10^{11}. For reactions (b) a statistical mechanical calculation of P is difficult and thus it is possible a priori that C falls below the gas value by several powers of ten.

This possibility can be tested by comparison of the kinetics of the following diene syntheses : (1) benzoquinone + *cyclo*pentadiene ; (2) *cyclo*pentadiene-benzoquinone + *cyclo*pentadiene ; (3) *cyclo*pentadiene + *cyclo*pentadiene ; (4) α-naphthoquinone + *cyclo*pentadiene ; (5) acrolein + *cyclo*pentadiene ; (6) acrolein + isoprene ; (7) acrolein + butadiene ; (8) crotonic aldehyde + butadiene. 1–4 were examined in solution[3] and 5–8 in the gaseous state[4]. All are homogeneous bimolecular associations of the type $a + b \rightarrow c$, and all obey the Arrhenius equation. The values for Z and E are given in the accompanying table. It will be observed that for all the eight reactions Z is of the order 10^6, whether in the gas phase or in solution.

Reaction	Formula of Reactants	$Z \times 10^{-6}$ (1/gm.-mol. sec.)	E (kgm. cal.)	
1	$C_6H_4O_2 + C_5H_6$	2·5[5]	11·6[5]	
2	$C_{11}H_{10}O_2 + C_5H_6$	0·33	13·2	Benzene
3	$C_5H_6 + C_5H_6$	1·2	16·4	Solution
4	$C_{10}H_6O_2 + C_5H_6$	0·06	10·0	
5	$C_3H_4O + C_5H_6$	1·5	15·2	
6	$C_3H_4O + C_5H_8$	1·0	18·7	Gaseous
7	$C_3H_4O + C_4H_6$	1·5	19·7	State
8	$C_4H_6O + C_4H_6$	0·9	22·0	

For the bimolecular associations in the gaseous state (5–8), C must be $\sim 10^{11}$ and therefore $P \sim 10^{-5}$. This small steric factor is explicable by reference to the passage of translational and rotational degrees of freedom of the reactants into vibrational degrees of freedom of the 'intermediate configuration'.

The molecules involved in the diene syntheses in solution are more complex than those involved in the gaseous reactions. For the associations here considered a larger number of degrees of freedom of the reactants will have the effect of either decreasing the steric factor P or leaving it unchanged. It follows that for 1–4 the upper limit of P is $\sim 10^{-5}$, and C at least 10^{11}. Hence for 'slow' reactions (type b) the collision frequency is not lower than that obtaining in the gas phase.

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[1] Moelwyn-Hughes and Hinshelwood, *J. Chem. Soc.*, 230 (1932); Moelwyn-Hughes, *Chem. Rev.*, **10**, 241 (1932); "Kinetics of Reaction in Solution", Oxford (1933).
[2] Cf. papers mentioned in the footnote of the preceding letter.
[3] Wassermann, *Ber.*, **66**, 1392 (1933); NATURE, **134**, 101 (1934); *J. Chem. Soc.*, 828, 1511 (1935); *Trans. Farad. Soc.*, **62**, 69 (1936) and preceding letter.
[4] Kistiakowsky and Lacher, *J. Amer. Chem. Soc.*, **58**, 123 (1936).
[5] These figures have been calculated from measurements over a larger temperature interval than those in *Ber.* and *J. Chem. Soc.*, loc. cit.

Diamagnetic Susceptibility of Heavy Water

THE diamagnetic susceptibility of heavy water has been measured by Selwood and Frost[1] using a specimen only 92 per cent pure, and by Cabrera and Fahlenbrach[2] with a 99 per cent pure specimen. A specimen of 99·2 per cent purity having recently become available, it was thought worth while to measure the susceptibility by Gouy's method, using apparatus already set up for other investigations of which details have appeared elsewhere[3]. Two specimen tubes were used containing approximately 1·32 gm. and 1·01 gm. of ordinary water to their respective filling marks. The procedure was to take a reading with ordinary water in the tube and then with heavy water. Equal volumes of ordinary and heavy water were delivered into the tube from a specially constructed pipette. In this way measurements were made upon three samples in each tube, the mean results being $0.649 \pm 0.001(3)$ and $0.649 \pm 0.001(0)$ in units of 10^{-6}, for the two tubes, obtained by taking the susceptibility of ordinary water to be 0·720 at 20° C. The final mean value, corrected for the presence of ordinary water, is $0.648 \pm 0.001(2)$ at 20° C. ; the average deviation from the mean is given in each case.

This result is higher than that of Cabrera and Fahlenbrach, 0·637 at 20° C., and also that obtained by Selwood and Frost, whose result of 0·65 for a specimen 92 per cent pure, if extrapolated to a 100 per cent purity assuming a linear variation with percentage composition, corresponds to a susceptibility of 0·644.

Taking the molecular weight of heavy water to be 20·027, we have 12·96 for its molecular susceptibility from the results of the present investigation ; the molecular susceptibility of ordinary water at the same temperature is 12·97.